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THEORETICAL STUDIES
ON
CHEMICAL REACTIVITIES
AND
PHYSICOCHEMICAL PROPERTIES
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HYDROCARBONS AND THEIR DERIVATIVES

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CONTENTS

PREFACE	vi
ACKNOWLEDGMENT	vii
PART I THEORETICAL STUDIES ON CHEMICAL REACTIVITIES.		
Chapter 1. Introduction	
Chapter 2. LCAO MO Perturbation Treatment of Conjugated Molecules	
§1. Introduction	
§2. Summary of Results for Single Perturbation...		
§3. Changes of Two Coulomb Integrals	1
§4. Changes of a Coulomb Integral and a Resonance Integral	18
§5. A Weak Bonding with a Change of a Coulomb Integral	21
§6. Weak Bondings to Two Conjugated Systems	24
§7. More General Case of Many Perturbations	28
§8. Degenerate Systems	31
§9. Discussion	31
Chapter 3. Reactivity Indexes in SCF Method	36
§1. Introduction	36
§2. LCAO SCF Calculation on Anthracene	37
§3. SCF Reactivity Indexes and Discussion	39

Chapter 4.	Localization Energy with Electronic Interaction	47
§1.	Introduction	47
§2.	Model of Localized Systems	48
§3.	Formulation and Evaluation of Atomic Integrals	49
§4.	Results and Discussion	56
Chapter 5.	Frontier Electron Theory and Z Value	64
§1.	Introduction		64
§2.	Mathematical Interrelation between Superdelocalizability and Z Value---- Heterolytic Reaction	67
§3.	Mathematical Interrelation between Superdelocalizability and Z Value--- Homolytic Reaction	72
§4.	Discussions on Charge Transfer Mechanism of Aromatic Substitution	75
Chapter 6.	Molecular Orbital Theory of Reactivities of Excited Molecules	84
§1.	Introduction	84
§2.	Reaction of an Excited Triplet Molecule with an Unexcited Radical	86
§3.	Reactions of an Excited Triplet Molecule with an Unexcited Molecule	95
§4.	Some Other Kinds of Reaction	101
§5.	Discussion	103

Chapter 7.	On Cross Termination in Radical Polymerization	110
§1.	Introduction	110
§2.	Calculation of π Conjugation Energy and Results and Discussion	112
Chapter 8.	Electronic Structures and Antioxidizing Activities	117
§1.	Introduction	117
§2.	π Electronic Structures and Antioxidizing Activities of Substituted Phenols	118
§3.	σ Electronic Structures and Antioxidizing Activities of Phenols	124
§4.	Discussion	130
PART II	THEORETICAL STUDIES OF PHYSICOCHEMICAL PROPERTIES	142
Chapter 1.	Introduction	143
Chapter 2.	Sigma Electronic Structures and Some Physicochemical Properties of Halogenated Conjugated Hydrocarbons	147
§1.	Introduction	147
§2.	Method of Calculation and Evaluation of Parameters	148
§3.	Results of Calculation and Their General Properties	149
§4.	Effects of Parameters	150
§5.	Effects of Overlap Integrals	151
§6.	Dipole Moments	152

§7.	Coupling Constants of Halogen in Pure Quadrupole Resonance Spectra	153
Chapter 3.	Polarographic Reduction and Electronic Structures of Organic Halides	175
§1.	Introduction	175
§2.	Method of Calculation	178
§3.	Polarographic Reduction and σ Electronic Structures of Haloalkanes	180
§4.	Polarographic Reduction and π and σ Electronic Structures of Conjugated Halides	183
§5.	Possible Inversion of Height of Energy Levels and $\pi \rightarrow \sigma^*$ Transition	185
§6.	Discussion	187
Chapter 4.	Electronic Spectra of Polyhalogenated Conjugated Hydrocarbons	195
§1.	Introduction	195
§2.	Theoretical Method and Approximate Evaluation of Atomic Integrals	197
§3.	The Lowest $\pi \rightarrow \pi^*$ and the Lowest $\pi \rightarrow \sigma^*$ Transitions in Tetrachloroethylene	204
§4.	Discussion	208
Chapter 5.	A Simple Molecular Orbital Method for Computing σ and π Electronic Structures with Unificative Parameters	225
§1.	Introductory Discussion	225
§2.	Choice of New Set of Parameters	229
§3.	Calculated Results and Discussion	236

Chapter 6.	Electronic Spectra and Some Physicochemical Properties of Anthracene	243
§1.	Introduction	243
§2.	Ionization Potential	244
§3.	Bond Order and Bond Distance	245
§4.	Electronic Spectra	245
Chapter 7.	A Simple Molecular Orbital Method for Discussing Electronic Structures of Stereoisomers-----Theoretical Method and ESR Hyperfine Splittings of Terephthalaldehyde Anion	250
§1.	Introduction	250
§2.	Theoretical Method	252
§3.	ESR Hyperfine Splittings of Terephthalaldehyde Anion	257
Chapter 8.	Angular Dependency of ESR Proton Hyperfine Coupling Constant of CH ₂ Group	270
§1.	Introduction	270
§2.	Model of Calculation	273
§3.	Result and Discussion	279
§4.	Application to Allyl Type Radical in Oriented Polyethylene	282
Chapter 9.	Theoretical Assignment of ESR Spectra of Cyclohexadienyl C ₆ H ₇ · and Phenyl C ₆ H ₅ · Radicals	297
§1.	Introduction	297
§2.	Valence Bond Calculation of Proton Coupling Constants in Cyclohexadienyl Radical.....		299

§3.	Valence Bond Calculation of Proton Coupling Constants in Phenyl Radical.....	303
§4.	Assignment of Observed Spectra and Discussion	306
Chapter 10.	Valence Bond Calculation of Spin Densities of Various Hydrocarbon Radical in a Simplest Approximation	316
§1.	IntroducTiōn	316
§2.	Approximation and General Results	317
§3.	Some Examples	321
CLOSING	331

PREFACE

Since Hettler and London's famous work in 1927 on the homopolar bond between hydrogens, the quantum mechanics, especially, the valence bond method by Pauling and Slater and the molecular orbital method by Hückel and Mulliken have enabled us to obtain theoretical view-points on complicated phenomena in chemistry. Application of quantum mechanics to organic chemistry has been made mainly in two fields. One of them is the field of the chemical reactivities, which are the most essential problems in organic chemistry. The other is the field of several kinds of molecular spectroscopy and other physicochemical measurements. Some of the new spectroscopies are essentially based on the quantum mechanics and cannot be treated without it.

The present thesis, which has been prepared under the direction of Professor Kenichi Fukui, is divided into two parts. In Part I theoretical studies on chemical reactivities of hydrocarbons and their derivatives are presented. In Part II theoretical studies on physicochemical properties measured by several spectroscopies are submitted. The both parts together, supplementing each other, will have a more exact meaning than each part alone.

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PART I

THEORETICAL STUDIES

ON CHEMICAL REACTIVITIES

Chapter 1

Introduction

The frontier electron theory by Fukui and his co-workers has achieved brilliant successes not only in establishing theoretical bases on the mechanism of aromatic substitution reaction¹⁻⁶⁾ but in interpreting several addition reactions⁷⁾, in discussing reactivities of monomers, radicals and ions in vinyl polymerization reactions⁸⁻¹⁰⁾ and reactivities saturated compounds¹¹⁻¹⁴⁾ and in many other fields of chemical reactions.¹⁵⁻¹⁸⁾ In this part of the thesis, the author wishes to present some molecular orbital results on chemical reactivities according to the frontier electron theory.

In Chapter 2 (published in the Bulletin of the Chemical Society of Japan, 33, 963 (1960)) is given a perturbation theory of the simple molecular orbital method for systems which are suffered by many kinds of perturbation at the same time. The results will be useful for various discussions not only on chemical reactivities but on physicochemical properties.

In Chapter 3 (published in the Bulletin of the Chemical Society of Japan, 32, 853 (1959)) and in Chapter 4 (published

in the Bulletin of the Chemical Society of Japan, 32, 1015 (1959)) some reactivity indexes of simple molecular orbital method----total π electron density, free valence, frontier electron density and localization energy----are re-examined in higher approximations in which the interaction between electrons is explicitly taken into account.

In Chapter 5 (published in the Journal of Chemical Physics, 32, 1743 (1960)) are found mathematical inter-relations between superdelocalizability and the Z value, i.e., two of the reactivity indexes of conjugated molecules. Molecular orbital theoretical discussions on the mechanism of aromatic substitution are also made.

In Chapter 6 (published in the Bulletin of the Chemical Society of Japan, 34, 1178 (1961)) is presented a molecular orbital theory of reactivities of excited conjugated molecules in photodimerization and photopolymerization reactions.

In the last two chapters application of the frontier electron theory to some special topics is given. In Chapter 7 (published in Journal of Polymer Science, 49, S11 (1961)) is discussed the ease of cross termination reaction in radical polymerization of vinyl compounds. In Chapter 8 (in press in the Bulletin of the Chemical Society of Japan, 36, (1963)) antioxidizing activities of phenols are connected to reactivity indexes of σ electron systems

as well as of π electron systems.

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Chapter 2

Simple LCAO MO Perturbation Treatment of Conjugated Molecules

§1. Introduction

The perturbation theory in the simple LCAO MO (linear-combination-of-atomic-orbital molecular orbital) method has been studied by many authors, for instance, by Coulson and Longuet-Higgins¹⁾ and by Dewar²⁾. Recently, by the present authors³⁾, a new mathematical method of perturbation theory, named the method of perturbed secular determinant, has been developed and several useful equations have been derived which give the orbital energy, the electron density and the bond order of the perturbed system.

The only system involved in these works, however, was the one which suffered only one perturbation, that is, a small change of a Coulomb integral or of a resonance integral, or a weak bonding to another system. There could be seen no systematic perturbation treatment of the system which was affected by two or more perturbations, for instance, changes of two Coulomb integrals, changes of a Coulomb integral and of a resonance integral, and a weak bonding with a change of a Coulomb integral. To deal with such a system would be of practical interest in discussing the chemical reactivity,

absorption spectrum, dipole moment and other electronic properties of large conjugated molecules.

In the present chapter are derived several equations or relations which give the molecular orbital, its orbital energy, the electron density and the bond order of systems affected by two perturbations, and lastly they are extended to a more general case of many perturbations.

§2. Summary of Results for Single Perturbation

In order to simplify the expression of various equations appearing in the treatment of multiple-perturbed systems, it would be convenient to summarize the results for single perturbation. The following formulae, obtained by the method of perturbed secular determinant and also by the existing method of perturbation, were given in the previous paper, though some of them not explicitly.

In this section it is assumed that the system to be treated is not degenerate in itself, nor has it any degenerate level between another system to conjugate with.

First, if the Coulomb integral, α_r , of the r th atom in a conjugated system, $\Delta(\epsilon)^*$, is increased by α'_r (Case A

* $\Delta(\epsilon)$ is the secular determinant of the system and will be used also to characterize a conjugated system.

of Ref. 3), then, as its consequence, the j th orbital energy, ϵ_j , will increase by $(\delta\epsilon_j)_r$, the separate bond order, p_{uvi} , by $(\delta p_{uvi})_r$, the separate electron density, p_{uu}^i , by $(\delta p_{uu}^i)_r$, the total π electronic energy, ϵ , by $(\delta\epsilon)_r$, the bond order, p_{uv} , by $(\delta p_{uv})_r$, the electron density, p_{uu} , by $(\delta p_{uu})_r$ and the j th molecular orbital, ψ_j , by $(\delta\psi_j)_r$, in such a way that*

$$(\delta\epsilon_j)_r = (C_r^j)^2 \alpha_r' + \sum_{k(\neq j)}^{all} \frac{(C_r^j C_r^k)^2}{\epsilon_j - \epsilon_k} (\alpha_r')^2 + \dots \quad (1)$$

$$\begin{aligned} (\delta p_{uv}^j)_r = & \sum_{k(\neq j)}^{all} \frac{C_r^j C_r^k (C_u^j C_v^k + C_v^j C_u^k)}{\epsilon_j - \epsilon_k} \alpha_r' \\ & + \sum_{k(\neq j)}^{all} \frac{C_r^j C_r^k}{\epsilon_j - \epsilon_k} \left[\sum_{m(\neq j)}^{all} \frac{C_r^m \{C_r^j C_u^k C_v^m + C_r^m (C_u^j C_v^k + C_v^j C_u^k)\}}{\epsilon_j - \epsilon_m} \right. \\ & \left. - \frac{C_r^j \{C_r^k C_u^j C_v^j + C_r^j (C_v^j C_u^k + C_v^j C_u^k)\}}{\epsilon_j - \epsilon_k} \right] (\alpha_r')^2 + \dots \quad (2) \\ & (u=v \text{ or } u \neq v) \end{aligned}$$

$$(\delta\epsilon)_r = p_{rr} \alpha_r' + 2 \sum_j^{occ} \sum_k^{unocc} \frac{(C_r^j C_r^k)^2}{\epsilon_j - \epsilon_k} (\alpha_r')^2 + \dots \quad (3)$$

$$\begin{aligned} (\delta p_{uv})_r = & 2 \sum_j^{occ} \sum_k^{unocc} \frac{C_r^j C_r^k (C_u^j C_v^k + C_v^j C_u^k)}{\epsilon_j - \epsilon_k} \alpha_r' \\ & + 2 \sum_j^{occ} \{ \text{the second order term in } (\delta p_{uv}^j)_r \} + \dots \quad (u=v \text{ or } u \neq v) \quad (4) \end{aligned}$$

$$(\delta\psi_j)_r = \sum_{k(\neq j)}^{all} \frac{C_r^j C_r^k}{\epsilon_j - \epsilon_k} \alpha_r' \psi_k - \frac{1}{2} \left\{ \sum_{k(\neq j)}^{all} \frac{(C_r^j C_r^k)^2}{(\epsilon_j - \epsilon_k)^2} \right\} (\alpha_r')^2 \psi_j$$

* As for the nomenclature, see Ref. 3. Electron density will be looked upon as a special case ($u=v$) of bond order in the further discussion.

$$+ \sum_{k(\neq j)}^{all} \frac{C_s^j C_t^k}{\varepsilon_j - \varepsilon_k} \left\{ \sum_{m(\neq j)}^{all} \frac{(C_r^m)^2}{\varepsilon_j - \varepsilon_m} - \frac{(C_r^j)^2}{\varepsilon_j - \varepsilon_k} \right\} (\alpha_r')^2 \psi_k + \dots \quad (5)$$

Secondly, when the resonance integral, β_{st} , of the bond (st) in the system $\Delta(\varepsilon)$ is increased by β_{st}' (Case B of Ref. 3), increases of those quantities are written as follows:

$$(\delta \varepsilon_j)_{st} = 2C_s^j C_t^j \beta_{st}' + \sum_{k(\neq j)}^{all} \frac{(C_s^j C_t^k + C_t^j C_s^k)^2}{\varepsilon_j - \varepsilon_k} (\beta_{st}')^2 + \dots \quad (6)$$

$$\begin{aligned} (\delta p_{uv})_{st} = & \sum_{k(\neq j)}^{all} \frac{(C_s^j C_t^k + C_t^j C_s^k)(C_u^j C_v^k + C_v^j C_u^k)}{\varepsilon_j - \varepsilon_k} \beta_{st}' \\ & + \sum_{k(\neq j)}^{all} \frac{(C_s^j C_t^k + C_t^j C_s^k)}{\varepsilon_j - \varepsilon_k} \left\{ \sum_{m(\neq j)}^{all} \frac{(C_s^j C_t^m + C_t^j C_s^m)(C_u^k C_v^m + (C_s^k C_t^m + C_t^k C_s^m)(C_u^j C_v^m + C_v^j C_u^m))}{\varepsilon_j - \varepsilon_m} \right. \\ & \left. - \frac{(C_s^j C_t^k + C_t^j C_s^k)(C_u^j C_v^j + 2C_s^j C_t^j (C_u^j C_v^k + C_v^j C_u^k))}{\varepsilon_j - \varepsilon_k} \right\} (\beta_{st}')^2 + \dots \quad (u=v \text{ or } u \neq v) \quad (7) \end{aligned}$$

$$(\delta \varepsilon)_{st} = 2p_{st} \beta_{st}' + 2 \sum_j^{occ} \sum_k^{unocc} \frac{(C_s^j C_t^k + C_t^j C_s^k)^2}{\varepsilon_j - \varepsilon_k} (\beta_{st}')^2 + \dots \quad (8)$$

$$\begin{aligned} (\delta p_{uv})_{st} = & 2 \sum_j^{occ} \sum_k^{unocc} \frac{(C_s^j C_t^k + C_t^j C_s^k)(C_u^j C_v^k + C_v^j C_u^k)}{\varepsilon_j - \varepsilon_k} \beta_{st}' \\ & + 2 \sum_j^{occ} \{ \text{the second order term in } (\delta p_{uv})_{st} \} + \dots \quad (u=v \text{ or } u \neq v) \quad (9) \end{aligned}$$

$$\begin{aligned} (\delta \psi_j)_{st} = & \sum_{k(\neq j)}^{all} \frac{(C_s^j C_t^k + C_t^j C_s^k)}{\varepsilon_j - \varepsilon_k} \beta_{st}' \psi_k - \frac{1}{2} \sum_{k(\neq j)}^{all} \frac{(C_s^j C_t^k + C_t^j C_s^k)^2}{(\varepsilon_j - \varepsilon_k)^2} (\beta_{st}')^2 \psi_j \\ & + \sum_{k(\neq j)}^{all} \frac{C_s^j C_t^k + C_t^j C_s^k}{\varepsilon_j - \varepsilon_k} \left\{ \sum_{m(\neq j)}^{all} \frac{C_s^k C_t^m + C_t^k C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{2C_s^j C_t^j}{\varepsilon_j - \varepsilon_k} \right\} (\beta_{st}')^2 \psi_k + \dots \quad (10) \end{aligned}$$

Thirdly, when a conjugated system, $\Delta(\varepsilon)$, conjugates at the r th atom through a weak bonding, whose resonance integral is r_r , with another conjugated system, whose secular determinant is $\Delta_1(\varepsilon)$, (Case C of Ref. 3), then the increases of molecular quantities by this perturbation are given by the following formulae. The orbital energy of the k th orbital ψ_{1k} of the system $\Delta_1(\varepsilon)$ is η_{1k} and the coefficient of the ξ th atomic orbital in that molecular orbital is written as d_{ξ}^{1k} .

$$(\delta\varepsilon_j)_{r\xi} = \sum_k \frac{all (C_r^j d_{\xi}^{1k})^2}{\varepsilon_j - \eta_{1k}} (r_r)^2 + \left\{ \sum_k \frac{all (C_r^j d_{\xi}^{1k})^2}{\varepsilon_j - \eta_{1k}} \left[\sum_k \frac{(d_{\xi}^{1k})^2}{\varepsilon_j - \eta_{1k}} \left\{ \sum_{m(\neq j)} \frac{(C_r^m)^2}{\varepsilon_j - \varepsilon_m} - \frac{(C_r^j)^2}{\varepsilon_j - \eta_{1k}} \right\} \right] \right\} (r_r)^4 + \dots \quad (11)$$

$$(\delta p_{uv}^j)_{r\xi} = \sum_k \frac{all C_r^j d_{\xi}^{1k}}{\varepsilon_j - \eta_{1k}} \left\{ \sum_{m(\neq j)} \frac{C_r^m d_{\xi}^{1k} (C_u^j C_v^m + C_v^j C_u^m)}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j d_{\xi}^{1k} C_u^j C_v^j}{\varepsilon_j - \eta_{1k}} \right\} (r_r)^2 + \dots$$

$$(u=v \text{ or } u \neq v) \quad (12)$$

$$(\delta p_{\xi^j})_{r\xi} = \sum_k \frac{all (C_r^j d_{\xi}^{1k})^2}{\varepsilon_j - \eta_{1k}} r_r + 2 \sum_k \sum_n \frac{all (C_r^j d_{\xi}^{1k} d_{\xi}^{1n})^2}{(\varepsilon_j - \eta_{1k})(\varepsilon_j - \eta_{1n})} \left\{ \sum_{m(\neq j)} \frac{(C_r^m)^2}{\varepsilon_j - \varepsilon_m} - \frac{(C_r^j)^2}{\varepsilon_j - \eta_{1k}} \right\} (r_r)^3 + \dots \quad (12')$$

$$(\delta p_{uv}^{1k})_{r\xi} = \sum_j \sum_m \frac{all C_r^j C_r^m (d_{\xi}^{1k})^2 C_u^j C_v^m}{(\eta_{1k} - \varepsilon_j)(\eta_{1k} - \varepsilon_m)} (r_r)^2 + \dots \quad (u=v \text{ or } u \neq v) \quad (13)$$

$$\begin{aligned} (\delta \psi_j)_{r\xi} = & \sum_k \frac{all C_r^j d_{\xi}^{1k}}{\varepsilon_j - \eta_{1k}} r_r \psi_k - \frac{1}{2} \sum_k \frac{all (C_r^j d_{\xi}^{1k})^2}{(\varepsilon_j - \eta_{1k})^2} (r_r)^2 \psi_j \\ & + \sum_{m(\neq j)} \frac{all C_r^j C_r^m}{\varepsilon_j - \varepsilon_m} \sum_k \frac{all (d_{\xi}^{1k})^2}{\varepsilon_j - \eta_{1k}} (r_r)^2 \psi_m + \dots \end{aligned} \quad (14)$$

where the atom u and the bond (uv) are in the system $\Delta(\xi)$, and ξ is the position of weak conjugation in the system $\Delta'(\varepsilon)$. Similar formulae would be obtained for the system $\Delta'(\varepsilon)$. Thus the change of bond order and that of electron density and total π electronic energy change of the combined system are obtained as follows:

$$\begin{aligned}
 (\delta\varepsilon)_{r\xi} &= 2 \sum_j^{occ} (\delta\varepsilon_j)_{r\xi} + 2 \sum_k^{occ} (\delta\eta_{lk})_{r\xi} \\
 &= 2 \left(\sum_j^{occ} \sum_k^{unocc} - \sum_j^{unocc} \sum_k^{occ} \right) \frac{(C_r^j d_\xi^{lk})^2}{\varepsilon_j - \eta_{lk}} (r_r)^2 + 2 \sum_j^{occ} \{ \text{the fourth order term in } (\delta\varepsilon_j)_{r\xi} \} \\
 &\quad + 2 \sum_k^{occ} \{ \text{the fourth order term in } (\delta\eta_{lk})_{r\xi} \} + \dots
 \end{aligned} \tag{15}$$

$$\begin{aligned}
 (\delta\rho_{uv})_{r\xi} &= 2 \sum_j^{occ} (\delta\rho_{uv}^j)_{r\xi} + 2 \sum_k^{occ} (\delta\rho_{uv}^{lk})_{r\xi} \\
 &= 2 \left(\sum_k^{occ} \sum_j^{unocc} - \sum_k^{unocc} \sum_j^{occ} \right) \left[\frac{(d_\xi^{lk})^2}{\varepsilon_j - \eta_{lk}} \left\{ \frac{(C_r^j)^2 C_u^j C_v^j}{\varepsilon_j - \eta_{lk}} \right. \right. \\
 &\quad \left. \left. - \sum_{m(\neq j)}^{all} \frac{C_r^j C_r^m (C_u^j C_v^m + C_v^j C_u^m)}{\varepsilon_j - \varepsilon_m} \right\} \right] (r_r)^2 + \dots \quad (u=v \text{ or } u \neq v)
 \end{aligned} \tag{16}$$

$$\begin{aligned}
 (\delta\rho_{r\xi})_{r\xi} &= 2 \left(\sum_j^{occ} \sum_k^{unocc} - \sum_j^{unocc} \sum_k^{occ} \right) \frac{(C_r^j d_\xi^{lk})^2}{\varepsilon_j - \eta_{lk}} r_r + 2 \sum_j^{occ} \{ \text{the third order term in } (\delta\rho_{r\xi}^j)_{r\xi} \} \\
 &\quad + 2 \sum_k^{occ} \{ \text{the third order term in } (\delta\rho_{r\xi}^{lk})_{r\xi} \} + \dots
 \end{aligned} \tag{16'}$$

Here it was assumed that the highest occupied orbitals of the systems $\Delta'(\varepsilon)$ and $\Delta(\varepsilon)$ are lower than the lowest

unoccupied orbitals of the systems $\Delta_1(\varepsilon)$ and $\Delta(\varepsilon)$, respectively. The total charge transfer, δQ , from the system $\Delta_1(\varepsilon)$ to the system $\Delta(\varepsilon)$ is defined by

$$\delta Q = \sum_{u=1}^n \delta p_{uu} \quad (17)$$

where n is the number of atomic orbitals in the system $\Delta(\varepsilon)$.

For this case δQ is given by the following equation.

$$(\delta Q)_{r\bar{k}} = 2 \left(\sum_k^{\text{occ}} \sum_j^{\text{unocc}} - \sum_k^{\text{unocc}} \sum_j^{\text{occ}} \right) \frac{(c_r^j d_{\bar{k}}^{jk})^2}{(\varepsilon_j - \eta_{\bar{k}})^2} (r_r)^2 + \dots \quad (18)$$

As a special case involved in the Case C, when the system $\Delta_1(\varepsilon)$ is an atom or a mesomeric group, X, Eqs. 11 to 16 and 18 become

$$\begin{aligned} (\delta \varepsilon_j)_{rX} &= \frac{(c_r^j)^2}{\varepsilon_j - \alpha_X} (r_r)^2 + \frac{(c_r^j)^2}{\varepsilon_j - \alpha_X} \left\{ -\frac{(c_r^j)^2}{(\varepsilon_j - \alpha_X)^2} \right. \\ &\quad \left. + \sum_{m(\neq j)}^{all} \frac{(c_r^m)^2}{(\varepsilon_j - \alpha_X)(\varepsilon_j - \varepsilon_m)} \right\} (r_r)^4 + \dots \end{aligned} \quad (11-a)$$

$$(\delta \alpha_X)_{rX} = \sum_j^{all} \frac{(c_r^j)^2}{\alpha_X - \varepsilon_j} (r_r)^2 + \left\{ \sum_j^{all} \frac{(c_r^j)^2}{\alpha_X - \varepsilon_j} \right\} \left\{ -\sum_j^{all} \frac{(c_r^j)^2}{(\alpha_X - \varepsilon_j)^2} \right\} (r_r)^4 + \dots \quad (11-b)$$

$$(\delta p_{uv}^j)_{rX} = \left\{ \sum_{m(\neq j)}^{all} \frac{c_r^j c_r^m (c_u^j c_v^m + c_u^m c_v^j)}{(\varepsilon_j - \varepsilon_m)(\varepsilon_j - \alpha_X)} - \frac{(c_r^j)^2 c_u^j c_v^j}{(\varepsilon_j - \alpha_X)^2} \right\} (r_r)^2 + \dots \quad (12-a)$$

$$(\delta p_{rx}^j)_{rX} = \frac{(c_r^j)^2}{\varepsilon_j - \alpha_X} r_r + \frac{2(c_r^j)^2}{(\varepsilon_j - \alpha_X)^2} \left\{ \sum_{m(\neq j)}^{all} \frac{(c_r^m)^2}{\varepsilon_j - \varepsilon_m} - \frac{(c_r^j)^2}{\varepsilon_j - \alpha_X} \right\} (r_r)^3 + \dots \quad (12'-a)$$

$$(\delta p_{uv}^x)_{rx} = \left\{ \sum_j^{all} \sum_m^{all} \frac{C_r^j C_r^m C_u^j C_v^m}{(\epsilon_j - \alpha_x)(\epsilon_m - \alpha_x)} \right\} (\gamma_r)^2 + \dots \quad (13-a)$$

$$(\delta p_{rx}^x)_{rx} = \sum_j^{all} \frac{(C_r^j)^2}{\alpha_x - \epsilon_j} \gamma_r - 2 \left\{ \sum_j^{all} \sum_m^{all} \frac{(C_r^j C_r^m)^2}{(\alpha_x - \epsilon_j)^2 (\alpha_x - \epsilon_m)} \right\} (\gamma_r)^3 + \dots \quad (13'-a)$$

$$(\delta p_{xx}^j)_{rx} = \frac{(C_r^j)^2}{(\epsilon_j - \alpha_x)^2} (\gamma_r)^2 + \dots \quad (12-b)$$

$$(\delta p_{xx}^x)_{rx} = - \sum_j^{all} \frac{(C_r^j)^2}{(\alpha_x - \epsilon_j)^2} (\gamma_r)^2 + \dots \quad (13-b)$$

$$(\delta p_{uv})_{rx} = \left(\nu \sum_j^{all} - 2 \sum_j^{occ} \right) \left\{ \frac{(C_r^j)^2 C_u^j C_v^j}{(\epsilon_j - \alpha_x)^2} + \sum_{m(\neq j)}^{all} \frac{C_r^j C_r^m (C_u^j C_v^m + C_v^j C_u^m)}{(\alpha_x - \epsilon_j)(\epsilon_j - \epsilon_m)} \right\} (\gamma_r)^2 + \dots \quad (16-a)$$

$$(\delta p_{xx})_{rx} = \left(2 \sum_j^{occ} - \nu \sum_j^{all} \right) \frac{(C_v^j)^2}{(\alpha_x - \epsilon_j)^2} (\gamma_r)^2 + \dots \quad (16-b)$$

$$(\delta p_{rx})_{rx} = \left(2 \sum_j^{occ} - \nu \sum_j^{all} \right) \frac{(C_r^j)^2}{\epsilon_j - \alpha_x} \gamma_r + 2 \sum_j^{occ} \left\{ \text{the third order term in } (\delta p_{rx}^j)_{rx} \right\} + \nu \left\{ \text{the third order term in } (\delta p_{rx}^x)_{rx} \right\} + \dots \quad (16'-a)$$

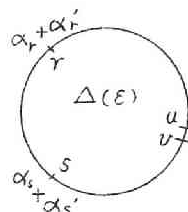
$$(\delta Q)_{rx} = \left(\nu \sum_j^{all} - 2 \sum_j^{occ} \right) \frac{(C_r^j)^2}{(\alpha_x - \epsilon_j)^2} (\gamma_r)^2 + \dots \quad (18-a)$$

where ν is the number of electrons in the atom X. The equations corresponding to Eqs. 14 and 15 are omitted for simplicity.

In the following sections some important cases of doubly perturbed systems will be treated.

§3. Changes of Two Coulomb Integrals

If two atoms, say the r th and the s th atoms, in a conjugated molecule, $\Delta(\epsilon)$, are replaced by two heteroatoms, the Coulomb integrals of these atoms will become $\alpha_r + \alpha_r'$ and $\alpha_s + \alpha_s'$, respectively. Then the perturbed secular determinant of the system will be written



$$D(\epsilon) = \Delta(\epsilon) + \alpha_r' \Delta_{rr}(\epsilon) + \alpha_s' \Delta_{ss}(\epsilon) + \alpha_r' \alpha_s' \Delta_{rrss}(\epsilon) \quad (19)$$

where $\Delta_{rr}(\epsilon)$ and $\Delta_{rrss}(\epsilon)$ are the (rr) minor and the (rr, ss) minor of $\Delta(\epsilon)$, respectively. Regarding these changes, α_r' and α_s' , as perturbations, one can easily obtain the perturbed orbital energy, of the j th molecular orbital, the perturbed bond order and the perturbed electron density by the use of the method of perturbed secular determinant, as will be briefly explained in the following.

First if one intermediately considers a system where α_s' is zero, the intermediate perturbed secular determinant is given as :

$$\square(\varepsilon) = \Delta(\varepsilon) + \alpha_r' \Delta_{rr}(\varepsilon) \quad (20)$$

According to the procedure utilized in the previous paper, the intermediate perturbed orbital energy, $\tilde{\varepsilon}_j$, and the intermediate perturbed separate bond order, $\tilde{\rho}_{uv}^j$, are expanded in powers of α_r' :

$$\left. \begin{aligned} \tilde{\varepsilon}_j &= \sum_{m=0}^{\infty} a_r^{j(m)} (\alpha_r')^m \\ \tilde{\rho}_{uv}^j &= \sum_{m=0}^{\infty} a_{r,uv}^{j(m)} (\alpha_r')^m \end{aligned} \right\} \quad (21)$$

and the coefficients, $a_r^{j(m)}$ and $a_{r,uv}^{j(m)}$, are given by the following formulae.

$$\begin{aligned} a_r^{j(m)} &= \frac{(-1)^m}{m!} \left[\frac{d^m}{dz^m} \frac{z \{ \Delta_{rr}(Z) \}^{m-1} \{ \Delta'(Z) \Delta_{rr}(Z) - \Delta(Z) \Delta_{rr}'(Z) \}}{\{ \Delta(Z)/(Z - \varepsilon_j) \}^{m+1}} \right]_{Z=\varepsilon_j} \\ &\quad (m = 0, 1, 2, \dots) \\ a_{r,uv}^{j(m)} &= \frac{(-1)^{m+1}}{m!} \left[\frac{d^m}{dz^m} \frac{\{ \Delta_{rr}(Z) \}^m \Delta_{uv}(Z) \Delta_{rv}(Z)}{\{ \Delta(Z)/(Z - \varepsilon_j) \}^{m+1}} \right]_{Z=\varepsilon_j} \\ &\quad (m = 0, 1, 2, \dots) \end{aligned} \quad (22)$$

Directly from these formulae the following expressions are obtained

$$\left. \begin{aligned} \tilde{\varepsilon}_j &= \varepsilon_j + (\delta \varepsilon_j)_r \\ \tilde{\rho}_{uv}^j &= \rho_{uv}^j + (\delta \rho_{uv}^j)_r \end{aligned} \right\} \quad (23)$$

where $(\delta \varepsilon_j)$ and $(\delta \rho_{uv}^j)$ are given by Eqs. 1 and 2.

Then the second perturbation, α_s' , is to be taken into account. The perturbed secular determinant of the system in question is expressed with the aid of the secular determinant of the intermediate system,

$$D(\varepsilon) = \square(\varepsilon) + \alpha_s' \square_{ss}(\varepsilon) \quad (24)$$

A similar procedure leads to the expansion formulae

$$\left. \begin{aligned} \varepsilon_j' &= \sum_{m=0}^{\infty} b_s^{j(m)} (\alpha_s')^m \\ \rho_{uv}^j &= \sum_{m=0}^{\infty} b_{s,uv}^{j(m)} (\alpha_s')^m \end{aligned} \right\} \quad (25)$$

where the coefficients, $b_s^{j(m)}$ and $b_{s,uv}^{j(m)}$, are the functions of α_s' and are given by

$$\left. \begin{aligned} b_s^{j(m)} &= \frac{(-1)^m}{m!} \left[\frac{d^m}{dz^m} \frac{Z \{ \square_{ss}(Z) \}^{m-1} \{ \square'(Z) \square_{ss}(Z) - \square(Z) \square_{ss}'(Z) \}}{\{ \square(Z) / (Z - \tilde{\varepsilon}_j) \}^{m+1}} \right]_{Z=\tilde{\varepsilon}_j} \\ &\quad (m=0, 1, 2, \dots) \\ b_{s,uv}^{j(m)} &= \frac{(-1)^{m+1}}{m!} \left[\frac{d^m}{dz^m} \frac{\{ \square_{ss}(Z) \}^m \square_{us}(Z) \square_{sv}(Z)}{\{ \square(Z) / (Z - \tilde{\varepsilon}_j) \}^{m+1}} \right]_{Z=\tilde{\varepsilon}_j} \\ &\quad (m=0, 1, 2, \dots) \end{aligned} \right\} \quad (26)$$

Thus we finally reach the following results for this perturbed system.

$$\varepsilon_j' = \varepsilon_j + (\delta \varepsilon_j)_r + (\delta \varepsilon_j)_s + 2 \sum_{k(\neq j)}^{all} \frac{c_r^j c_r^k c_s^j c_s^k}{\varepsilon_j - \varepsilon_k} \alpha_r' \alpha_s' + \dots \quad (27)$$

$$\begin{aligned}
P_{uv}^j = & p_{uv}^j + (\delta p_{uv}^j)_r + (\delta p_{uv}^j)_s \\
& + \left[\sum_{k(\neq j)}^{all} \sum_{m(\neq j)}^{all} \frac{C_r^j C_s^j (C_r^k C_s^m + C_s^k C_r^m) C_u^k C_v^m + C_r^m C_s^m (C_r^j C_s^k + C_s^j C_r^k) (C_u^j C_v^k + C_v^j C_u^k)}{(E_j - E_k)(E_j - E_m)} \right. \\
& \left. - \sum_{k(\neq j)}^{all} \frac{C_r^j C_s^j \{ (C_r^j C_s^k + C_s^j C_r^k) (C_u^j C_v^k + C_v^j C_u^k) + 2 C_r^k C_s^k C_u^j C_v^j \}}{(E_j - E_k)^2} \right] \alpha_r' \alpha_s' + \dots \quad (28)
\end{aligned}$$

where $(\delta E_j)_r$ and $(\delta p_{uv}^j)_r$ are the change of the orbital energy and the separate bond order (or the separate electron density) respectively, of the j th molecular orbital caused by the perturbation α_r' , as were given in Eqs. 1 and 2.

On inspection of Eqs. 27 and 28 it is clearly seen that, as concerns the first order terms, two perturbations have no effect upon each other and, therefore, the so-called "additivity rule" comes into being. That is to say, the change of the orbital energy, the bond order or the electron density caused by two perturbations is expressed by the mathematical sum of its changes caused by each perturbation. In the second order a cross term appears, which may become comparable in magnitude with the non-cross term and cannot be neglected. Also as for the total π electronic energy, the bond order and the electron density, which are expressed by the sum of corresponding separate quantity, the circumstances are the

same, as follows:

$$\varepsilon' = \varepsilon + (\delta\varepsilon)_r + (\delta\varepsilon)_s + 2 \sum_j^{\text{occ}} \sum_k^{\text{unocc}} \frac{C_r^j C_r^k C_s^j C_s^k}{\varepsilon_j - \varepsilon_k} \alpha_r' \alpha_s' + \dots \quad (29)$$

$$P_{uv} = p_{uv} + (\delta p_{uv})_r + (\delta p_{uv})_s + \sum_j^{\text{occ}} \{ \text{cross term of the order } \alpha_r' \alpha_s' \text{ in } P_{uv} \} + \dots \quad (30)$$

where $(\delta\varepsilon)_r$ and $(\delta p_{uv})_r$, given by Eqs. 3 and 4, are the changes of total π electronic energy and the bond order (or the electron density) respectively, caused by the perturbation α_r' . Eqs. 27 to 30 can also be derived by the existing method of perturbation.

The explicit expression of perturbed molecular orbital would be useful for some purposes. It is

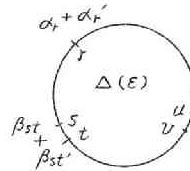
$$\begin{aligned} \psi_j' = & \psi_j + (\delta\psi_j)_r + (\delta\psi_j)_s - \sum_{k(\neq j)}^{\text{all}} \frac{C_r^j C_r^k C_s^j C_s^k}{(\varepsilon_j - \varepsilon_k)^2} \alpha_r' \alpha_s' \psi_j \\ & + \sum_{k(\neq j)}^{\text{all}} \frac{(C_r^j C_s^k + C_s^j C_r^k)}{\varepsilon_j - \varepsilon_k} \left\{ \sum_{m(\neq j)}^{\text{all}} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \varepsilon_k} \right\} \alpha_r' \alpha_s' \psi_k + \dots \end{aligned} \quad (31)$$

where $(\delta\psi_j)_r$ is given by Eq. 5.

§4. Changes of a Coulomb Integral and a Resonance Integral.

When at the same time the Coulomb integral of the r th atom is increased by α_r' and the resonance integral of the

bond (st), β_{st} , by β_{st}' , then the perturbed secular determinant of the system is expressed* by



$$D(\epsilon) = \Delta(\epsilon) + \alpha_r' \Delta_{rr}(\epsilon) + (-1)^{s+t} 2\beta_{st}' \Delta_{st}(\epsilon) - (\beta_{st}')^2 \Delta_{sstt}(\epsilon)$$

$$+ (-1)^{s+t} \alpha_r' \beta_{st}' \Delta_{rrst}(\epsilon) - \alpha_r' (\beta_{st}')^2 \Delta_{rrsst}(\epsilon)$$

(32)

As well as in Case I, the following expressions of the orbital energy, the separate bond order and the separate electron density are obtained.

$$\epsilon_j' = \epsilon_j + (\delta\epsilon_j)_r + (\delta\epsilon_j)_{st} + 2 \sum_{k(\neq j)} \frac{C_r^j C_r^k (C_s^j C_t^k + C_t^j C_s^k)}{\epsilon_j - \epsilon_k} \alpha_r' \beta_{st}' + \dots \quad (33)$$

$$P_{uv}^j = p_{uv}^j + (\delta p_{uv}^j)_r + (\delta p_u^j)_{st}$$

$$\begin{aligned} & + \left[\sum_{k(\neq j)} \frac{\sum_{m(\neq j)} C_r^j C_r^k (C_s^j C_t^m + C_t^j C_s^m) (C_u^k C_v^m + C_v^k C_u^m)}{(\epsilon_j - \epsilon_k)} \right. \\ & \quad \times \frac{\{C_r^k C_r^m (C_s^j C_t^m + C_t^j C_s^m) + C_r^m C_r^j (C_s^k C_t^m + C_t^k C_s^m)\} (C_u^j C_v^k + C_v^j C_u^k)}{(\epsilon_j - \epsilon_m)} \\ & \quad \left. - \sum_{k(\neq j)} \frac{2\{2C_r^j C_r^k C_s^j C_t^k + (C_s^j)^2 (C_s^k C_t^k + C_t^k C_s^k)\} (C_u^j C_v^k + C_v^j C_u^k) C_r^k C_r^k (C_s^j C_t^k + C_t^j C_s^k) C_u^j C_v^j}{(\epsilon_j - \epsilon_k)^2} \right] \alpha_r' \beta_{st}' \\ & + \dots \quad (34) \end{aligned}$$

* When $r = t$, though the perturbed secular determinant becomes $D(\epsilon) = \Delta(\epsilon) + \alpha_r' \Delta_{rr}(\epsilon) + (-1)^{s+r} 2\beta_{sr}' \Delta_{sr}(\epsilon) - (\beta_{sr}')^2 \Delta_{ssrr}(\epsilon)$, Eqs. 33 to 36 are valid.

where $(\delta \epsilon_j)_r$, $(\delta \epsilon_j)_{st}$, $(\delta p_{uv})_r$ and $(\delta p_{uv})_{st}$ are given by Eqs. 1, 6, 2 and 7, respectively. Also in this case a cross term between the two perturbations, both in the orbital energy and in the bond order (and the density), first arises in the second order, and therefore the additivity rule is correct in the first order. The circumstances are the same for the total energy, the bond order and the electron density.

$$\left. \begin{aligned} \epsilon' &= \epsilon + (\delta \epsilon)_r + (\delta \epsilon)_{st} \\ &+ 2 \sum_j^{\text{occ}} \{ \text{cross term of the order } \alpha_r' \beta_{st}' \text{ in } \epsilon_j \} + \dots \\ P_{uv} &= p_{uv} + (\delta p_{uv})_r + (\delta p_{uv})_{st} \\ &+ 2 \sum_j^{\text{occ}} \{ \text{cross term of the order } \alpha_r' \beta_{st}' \text{ in } p_{uv} \} \end{aligned} \right\} \quad (35)$$

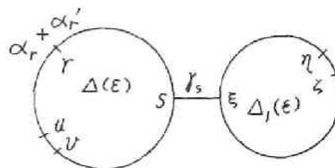
where $(\delta \epsilon)_{st}$ and (δp_{uv}) are given by Eqs. 8 and 9. The perturbed molecular orbital is obtained as follows:

$$\begin{aligned} \psi_j' &= \psi_j + (\delta \psi_j)_r + (\delta \psi_j)_{st} + \sum_{k(\neq j)}^{\text{all}} \left\{ \frac{\sum_{m(\neq j)}^{\text{all}} C_r^k C_r^m (C_s^j C_t^m + C_t^j C_s^m) + C_r^j C_r^m (C_s^k C_t^m + C_t^k C_s^m)}{(\epsilon_j - \epsilon_k)(\epsilon_j - \epsilon_m)} \right. \\ &\quad \left. - \frac{2 C_r^j C_r^k C_r^j C_t^j + (C_r^j)^2 (C_s^j C_t^k + C_t^j C_s^k)}{(\epsilon_j - \epsilon_k)^2} \right\} \alpha_r' \beta_{st}' \psi_k \\ &\quad - \sum_{k(\neq j)}^{\text{all}} \frac{C_r^j C_r^k (C_s^j C_t^k + C_t^j C_s^k)}{(\epsilon_j - \epsilon_k)^2} \alpha_r' \beta_{st}' \psi_j + \dots \end{aligned} \quad (36)$$

where $(\delta \psi_j)_{st}$ is given by Eq. 10.

§5. A Weak Bonding with a Change of a Coulomb Integral.

When a conjugated system, $\Delta(\varepsilon)$, conjugates at the S th atom through a weak bonding, whose resonance integral is γ_s , with another conjugated system $\Delta_1(\varepsilon)$, and at the same time the Coulomb integral of the r th atom is increased by α_r' , as illustrated in the figure, then the following formulae are obtained.



$$D(\varepsilon) = \Delta(\varepsilon)\Delta_1(\varepsilon) + \alpha_r' \Delta_{rr}(\varepsilon)\Delta_1(\varepsilon) - (\gamma_s)^2 \Delta_{ss}(\varepsilon)\Delta_{1\bar{s}\bar{s}}(\varepsilon)$$

$$- \alpha_r' (\gamma_s)^2 \Delta_{rrss}(\varepsilon) \Delta_{1\bar{s}\bar{s}}(\varepsilon) \quad (37)$$

$$\varepsilon_j' = \varepsilon_j + (\delta\varepsilon_j)_r + (\delta\varepsilon_j)_{s\bar{s}} + \sum_k \frac{C_r^j C_s^j (d_{\xi}^{jk})^2}{\varepsilon_j - \eta_{jk}} \left\{ 2 \sum_{m(\neq j)} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{jk}} \right\} \alpha_r' (\gamma_s)^2 + \dots \quad (38)$$

$$\eta_{jk}' = \eta_{jk} + (\delta\eta_{jk})_{s\bar{s}} + \sum_j \frac{C_r^j C_s^j (d_{\xi}^{jk})^2}{\eta_{jk} - \varepsilon_j} \left\{ 2 \sum_{m(\neq j)} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{jk}} \right\} \alpha_r' (\gamma_s)^2 + \dots \quad (39)$$

$$P_{uv}^j = p_{uv}^j + (\delta p_{uv}^j) + (\delta p_{uv}^j)_{s\bar{s}} + \{\text{cross term of the order } \alpha_r' (\gamma_s)^2\} + \dots \quad (40)$$

$$P_{s\xi}^j = (\delta p_{s\xi}^j)_{s\xi} + \sum_k \frac{C_r^j C_s^j (d_{\xi}^{jk})^2}{\varepsilon_j - \eta_{jk}} \left\{ 2 \sum_{m(k+j)} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{jk}} \right\} \alpha_r' \gamma_s + \dots \quad (40')$$

$$P_{uv}^{lk} = (\delta p_{uv}^{lk})_{s\xi} + \{ \text{cross term of the order } \alpha_r' (\gamma_s)^2 \} + \dots \quad (41)$$

$$P_{\eta\xi}^{lk} = p_{\eta\xi}^{lk} + (\delta p_{\eta\xi}^{lk})_{s\xi} + \{ \text{cross term of the order } \alpha_r' (\gamma_s)^2 \} + \dots \quad (42)$$

$$P_{s\xi}^{lk} = (\delta p_{s\xi}^{lk})_{s\xi} + \sum_j \frac{C_r^j C_s^j (d_{\xi}^{lk})^2}{\eta_{lk} - \varepsilon_j} \left\{ 2 \sum_{m(k+j)} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{lk}} \right\} \alpha_r' \gamma_s + \dots \quad (42')$$

$$P_{\eta\xi}^j = (\delta p_{\eta\xi}^j)_{s\xi} + \{ \text{cross term of the order } \alpha_r' (\gamma_s)^2 \} + \dots \quad (43)$$

where ξ is the position of weak conjugation in the system

$\Delta_r(\varepsilon)$, the bond $(\eta\xi)$ is in the system $\Delta_r(\varepsilon)$; and $(\delta\varepsilon_j)_{s\xi}$, $(\delta p_{uv}^j)_{s\xi}$, $(\delta p_{s\xi}^j)_{s\xi}$ and $(\delta p_{uv}^{lk})_{s\xi}$ are given by Eqs. 11, 12, 12' and 13, from which $(\delta\eta_{lk})_{s\xi}$, $(\delta p_{\eta\xi}^j)_{s\xi}$, $(\delta p_{\eta\xi}^{lk})_{s\xi}$ and $(\delta p_{s\xi}^{lk})_{s\xi}$ will easily be formulated.

Therefore the total π electronic energy of the combined system is

$$\begin{aligned} \varepsilon' = & \varepsilon + (\delta\varepsilon)_r + (\delta\varepsilon)_{s\xi} + 2 \left(\sum_j \sum_k^{\text{occ}} \frac{u_{jokc}}{u_{jokc}} - \sum_j \sum_k^{\text{occ}} \frac{u_{jokc}}{u_{jokc}} \right) \\ & \times \left[\frac{C_r^j C_s^j (d_{\xi}^{lk})^2}{\varepsilon_j - \eta_{lk}} \left\{ 2 \sum_{m(k+j)} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{lk}} \right\} \right] \alpha_r' \gamma_s + \dots \quad (44) \end{aligned}$$

And

$$P_{uv} = P_{uv} + (\delta p_{uv})_r + (\delta p_{uv})_{s\xi} + \{\text{cross term of the order } \alpha_r'(\gamma_s)^2\} + \dots \quad (45)$$

$$P_{s\xi} = (\delta p_{s\xi})_{s\xi} + 2 \left(\sum_j^{occ} \sum_k^{unocc} - \sum_j^{unocc} \sum_k^{occ} \right) \left[\frac{C_r^j C_s^j (d_{\xi}^{1/k})^2}{\epsilon_j - \eta_{1k}} \left\{ 2 \sum_{m(\neq j)}^{all} \frac{C_r^m C_s^m}{\epsilon_j - \epsilon_m} - \frac{C_r^j C_s^j}{\epsilon_j - \eta_{1k}} \right\} \right] \alpha_r' \gamma_s + \dots \quad (45')$$

$$P_{\eta\xi} = P_{\eta\xi} + (\delta p_{\eta\xi})_{s\xi} + \{\text{cross term of the order } \alpha_r'(\gamma_s)^2\} + \dots \quad (46)$$

$$\delta Q = (\delta Q)_{s\xi} + \{\text{cross term of the order } \alpha_r'(\gamma_s)^2\} + \dots \quad (47)$$

where $(\delta \epsilon)_{s\xi}$, $(\delta p_{uv})_{s\xi}$, $(\delta p_{s\xi})_{s\xi}$ and $(\delta Q)_{s\xi}$ are given by Eqs. 15, 16, 16' and 18. $(\delta p_{\eta\xi})_{s\xi}$ is easily written on inspection of Eq. 16. As is seen in Eqs. 45 to 47, a cross term first appears in the third order, that is, the order of $\alpha_r'(\gamma_s)^2$, and the additivity rule is valid up to the second order perturbation.

The wave functions of this perturbed system are re-presented by

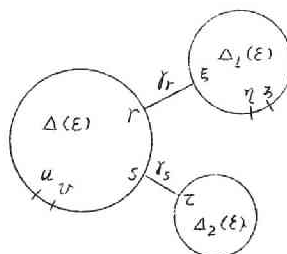
$$\psi_j' = \psi_j + (\delta \psi_j)_r + (\delta \psi_j)_{s\xi} + \sum_k^{all} \frac{C_r^j d_{\xi}^{1/k}}{\epsilon_j - \eta_{1k}} \left\{ \sum_{m(\neq j)}^{all} \frac{C_r^m C_s^m}{\epsilon_j - \epsilon_m} - \frac{C_r^j C_s^j}{\epsilon_j - \eta_{1k}} \right\} \alpha_r' \gamma_s \psi_{1k} + \dots \quad (48)$$

$$\psi_{1k}' = \psi_{1k} + (\delta\psi_{1k})_{s\xi} + \sum_j \frac{c_r^j d_{\xi}^{1k}}{\eta_{1k} - \varepsilon_j} \sum_{m(x_j)} \frac{c_r^m c_s^m}{\eta_{1k} - \varepsilon_m} \alpha_r' \gamma_s \psi_j + \dots \quad (49)$$

where $(\delta\psi_j)_{s\xi}$ is given by Eq. 14, from which also $(\delta\psi_{1k})_{s\xi}$ may easily be written.

§6. Weak Bondings to Two Conjugated Systems

Here we consider a case in which a conjugated system, $\Delta(\varepsilon)$, conjugates at the r th and the s th atoms with two other conjugated systems, $\Delta_1(\varepsilon)$ and $\Delta_2(\varepsilon)$, respectively, making weak bondings whose resonance integrals are γ_r and γ_s , respectively. The molecular orbital, its orbital energy and the coefficient of atomic orbital in the nonperturbed $\Delta_1(\varepsilon)$ system are designated by ψ_{1k} , η_{1k} and d_{μ}^{1k} , respectively, and in the system $\Delta_2(\varepsilon)$ by ψ_{2k} , η_{2k} and d_{ν}^{2k} . Then the following expressions are easily obtained for the perturbed combined system.



$$D(\varepsilon) = \Delta(\varepsilon) \Delta_1(\varepsilon) \Delta_2(\varepsilon) - (\gamma_r)^2 \Delta_{rr}(\varepsilon) \Delta_{1\xi\xi}(\varepsilon) \Delta_2(\varepsilon) \\ - (\gamma_s)^2 \Delta_{ss}(\varepsilon) \Delta_1(\varepsilon) \Delta_{2\tau\tau}(\varepsilon) + (\gamma_r \gamma_s)^2 \Delta_{rssi}(\varepsilon) \Delta_{1\xi\xi}(\varepsilon) \Delta_{2\tau\tau}(\varepsilon) \quad (50)$$

$$\varepsilon_j' = \varepsilon_j + (\delta\varepsilon_j)_{r\xi} + (\delta\varepsilon_j)_{s\tau} + \sum_k \frac{C_r^j (d_\xi^{1k})^2}{\varepsilon_j - \eta_{1k}} U_{jk} (\gamma_r \gamma_s)^2 + \dots \quad (51)$$

$$U_{jk} = \sum_l \frac{C_r^j (d_\tau^{2l})^2}{\varepsilon_j - \eta_{2l}} \left\{ 2 \sum_m \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{1k}} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{2l}} \right\} \quad (51'-a)$$

$$\eta_{1k}' = \eta_{1k} + (\delta\eta_{1k})_{r\xi} + \sum_j \frac{C_r^j (d_\xi^{1k})^2}{\eta_{1k} - \varepsilon_j} U_{jk} (\gamma_r \gamma_s)^2 + \dots \quad (52)$$

$$P_{uv}^j = p_{uv}^j + (\delta p_{uv}^j)_{r\xi} + (\delta p_{uv}^j)_{s\tau} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (53)$$

$$P_{r\xi}^j = (\delta p_{r\xi}^j)_{r\xi} + \sum_k \frac{C_r^j (d_\xi^{1k})^2}{\varepsilon_j - \eta_{1k}} U_{jk} \gamma_r (\gamma_s)^2 + \dots \quad (53')$$

$$P_{uv}^{1k} = (\delta p_{uv}^{1k})_{r\xi} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (54)$$

$$P_{r\xi}^{1k} = (\delta p_{r\xi}^{1k})_{r\xi} + \sum_j \frac{C_r^j (d_\xi^{1k})^2}{\eta_{1k} - \varepsilon_j} U_{jk} \gamma_r (\gamma_s)^2 + \dots \quad (54')$$

$$P_{uv}^{2l} = (\delta p_{uv}^{2l})_{s\tau} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (55)$$

$$P_{r\xi}^{2l} = \sum_k \frac{(d_\xi^{1k})^2}{\eta_{2l} - \eta_{1k}} \sum_j \sum_m \frac{C_r^j C_r^m C_s^j C_s^m (d_\tau^{2l})^2}{(\eta_{2l} - \varepsilon_j)(\eta_{2l} - \varepsilon_m)} \gamma_r (\gamma_s)^2 + \dots \quad (55')$$

$$P_{\eta\xi}^{1k} = p_{\eta\xi}^{1k} + (\delta p_{\eta\xi}^{1k})_{r\xi} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (56)$$

$$P_{\eta\xi}^j = (\delta p_{\eta\xi}^j)_{r\xi} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (57)$$

$$P_{\eta\xi}^{2l} = \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (58)$$

where ξ and τ are the positions of the weak conjugation in the systems $\Delta_1(\varepsilon)$ and $\Delta_2(\varepsilon)$, respectively, and the bond (uv) or the atom u is assumed to be in the system $\Delta_1(\varepsilon)$, and the bond $(\eta\zeta)$ or the atom η in the system $\Delta_2(\varepsilon)$. Similar expressions as above may be written for the system $\Delta_2(\varepsilon)$. Thus the total π electronic energy and the bond order of this perturbed system are given as follows:

$$\begin{aligned} \varepsilon' &= 2 \sum_j^{\text{occ}} \varepsilon_j' + 2 \sum_k^{\text{occ}} \eta_{1k}' + 2 \sum_l^{\text{occ}} \eta_{2l}' \\ &= \varepsilon + (\delta\varepsilon)_{r\xi} + (\delta\varepsilon)_{s\tau} \\ &\quad + \left\{ \sum_j^{\text{occ}} \left(\sum_k^{\text{unocc}} \sum_l^{\text{unocc}} - \sum_k^{\text{occ}} \sum_l^{\text{occ}} \right) - \sum_j^{\text{unocc}} \left(\sum_k^{\text{occ}} \sum_l^{\text{all}} + \sum_k^{\text{all}} \sum_l^{\text{occ}} \right) \right\} \frac{C_r^j C_s^j (d_\xi^{1k})^2 (d_\tau^{2l})^2}{(\varepsilon_j - \eta_{1k})(\varepsilon_j - \eta_{2l})} \\ &\quad \times \left(2 \sum_{m(\neq j)}^{\text{all}} \frac{C_r^m C_s^m}{\varepsilon_j - \varepsilon_m} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{1k}} - \frac{C_r^j C_s^j}{\varepsilon_j - \eta_{2l}} \right) (\gamma_r \gamma_s)^2 + \dots \end{aligned} \quad (59)$$

$$P_{uv} = P_{uv} + (\delta p_{uv})_{r\xi} + (\delta p_{uv})_{s\tau} + \{ \text{cross term of the order } (\gamma_r \gamma_s)^2 \} + \dots \quad (60)$$

$$\begin{aligned} P_{r\xi} &= (\delta p_{r\xi})_{r\xi} + \left[2 \left(\sum_j^{\text{occ}} \sum_k^{\text{unocc}} - \sum_j^{\text{unocc}} \sum_k^{\text{occ}} \right) \frac{C_r^j (d_\xi^{1k})^2}{\varepsilon_j - \eta_{1k}} U_{jk} \right. \\ &\quad \left. + 2 \sum_l^{\text{occ}} \sum_k^{\text{all}} \frac{(d_\xi^{1k})^2}{\eta_{2l} - \eta_{1k}} \sum_j^{\text{all}} \sum_m^{\text{all}} \frac{C_r^j C_r^m C_s^j C_s^m (d_\tau^{2l})^2}{(\eta_{2l} - \varepsilon_j)(\eta_{2l} - \varepsilon_m)} \right] \gamma_r (\gamma_s)^2 + \dots \end{aligned} \quad (60')$$

$$P_{\eta\xi} = P_{\eta\xi} + (\delta p_{\eta\xi})_{r\xi} + \{ \text{cross term of the order } (\gamma_r \gamma_s)^2 \} + \dots \quad (61)$$

The changes of total charge involved in the systems $\mathcal{A}(\varepsilon)$ and $\mathcal{A}_1(\varepsilon)$ are designated as δQ and δQ_1 , respectively, which are written as follows:

$$\delta Q = (\delta Q)_{r\xi} + (\delta Q)_{s\tau} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (62)$$

$$\delta Q_1 = (\delta Q)_{r\xi} + \{\text{cross term of the order } (\gamma_r \gamma_s)^2\} + \dots \quad (63)$$

A similar equation may be written also for the system $\mathcal{A}_2(\varepsilon)$

The molecular orbitals of this perturbed system are

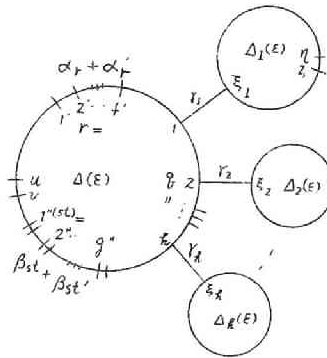
$$\begin{aligned} \psi_j' = \psi_j + (\delta\psi_j)_{r\xi} + (\delta\psi_j)_{s\tau} \\ + \{\text{cross term of the orders } \gamma_r(\gamma_s)^2 \text{ and } (\gamma_r)^2\gamma_s\} + \dots \end{aligned} \quad (64)$$

$$\phi_{ik}' = \phi_{ik} + (\delta\psi_{ik})_{r\xi} + \sum_j^{\text{all}} \sum_l^{\text{all}} \frac{C_r^j C_s^l d\xi^{ik} d\eta^{2l}}{(\eta_{ik} - \eta_{2l})(\eta_{ik} - \varepsilon_j)} \gamma_r \gamma_s \psi_{2k} + \dots \quad (65)$$

As to special cases in which either or both of the systems $\mathcal{A}_1(\varepsilon)$ and $\mathcal{A}_2(\varepsilon)$ are single atoms, one may simplify the results of Cases III and IV by using Eqs. 11-a to 18-a instead of Eqs. 11 to 18 for non-cross terms and by abridging cross terms.

§7. More General Case of Many Perturbations

Perturbation treatment of systems affected by two perturbations stated above may be extended to a more general case of many perturbations. As illustrated in the figure, we consider a conjugated system, $\Delta(\varepsilon)$, and increase the Coulomb integrals of the r th atoms in it ($r=1', 2', \dots, f'$) by $\alpha_{r'}$ and the resonance integrals of the bonds (st) ($st=1'', 2'', \dots, g''$) by $\beta_{st'}$, and make weak bondings, whose resonance integral is γ_q , between the q th atoms ($q=1, 2, \dots, h$) in the system and the ξ_q th atoms in other conjugated systems $\Delta_q(\varepsilon)$. Here some of the r 's, s 's and q 's may be the identical atoms.



Then the perturbed j th orbital energy of the system $\Delta(\varepsilon)$ is

$$\begin{aligned} \varepsilon_j' = \varepsilon_j + \sum_{r=1'}^{f'} (\delta \varepsilon_j)_r + \sum_{(st)=1''}^{g''} (\delta \varepsilon_j)_{st} + \sum_{q=1}^h (\delta \varepsilon_j)_{q\xi} \\ + C(\alpha^2, \alpha\beta, \beta^2) + C(\alpha^3, \alpha^2\beta, \alpha\beta^2, \beta^3, \alpha r^2, \beta r^2) \end{aligned}$$

$$+C(\alpha^4, \alpha^3\beta, \alpha^2\beta^2, \alpha\beta^3, \beta^4, \alpha^2r^2, \alpha\beta r^2, \beta^2r^2, r^4) + \dots \quad (66)$$

where $(\delta\varepsilon_j)_r$, $(\delta\varepsilon_j)_{st}$ and $(\delta\varepsilon_j)_{q\zeta}$ are energy changes caused by perturbations α_r , β_{st} and r_q , respectively, and are given by Eqs. 1, 6 and 11. and C means the cross term among perturbations. For instance $C(\alpha^2, \alpha\beta, \beta^2)$ consists of cross terms of orders $\alpha_1'\alpha_2'$, $\alpha_1'\alpha_3'$, \dots , $\alpha_2'\alpha_3'$, \dots , $\alpha_1'\beta_1'$, $\alpha_1'\beta_2'$, \dots , $\alpha_2'\beta_1'$, \dots , $\beta_1'\beta_2'$, $\beta_1'\beta_3'$, \dots , $\beta_2'\beta_3'$, \dots ; and $C(\alpha^3, \alpha^2\beta, \alpha\beta^2, \beta^3, \alpha r^2, \beta r^2)$ of orders $(\alpha_1')^2\alpha_2'$, \dots , $\alpha_1'\alpha_2'\alpha_3'$, \dots , $(\alpha_1')^2\beta_1'$, \dots , $\alpha_1'\alpha_2'\beta_1'$, \dots , $\alpha_1'(\beta_1')^2$, \dots , $\alpha_1'\beta_1'\beta_2'$, \dots , $(\beta_1')^2\beta_2'$, $\beta_1'\beta_2'\beta_3'$, \dots , $\alpha_1'(r_1)^2$, \dots , $\beta_1'(r_1)^2$, \dots .

The perturbed separate bond order by this orbital of the bond (uv) in the system $\Delta(\varepsilon)$ is

$$\begin{aligned} P_{uv}^j = & p_{uv}^j + \sum_{r=1}^{t'} (\delta p_{uv}^j)_r + \sum_{(st)=1}^{t''} (\delta p_{uv}^j)_{st} + \sum_{q=1}^h (\delta p_{uv}^j)_{q\zeta} \\ & + C(\alpha^2, \alpha\beta, \beta^2) + C(\alpha^3, \alpha^2\beta, \alpha\beta^2, \beta^3, \alpha r^2, \beta r^2) \\ & + C(\alpha^4, \alpha^3\beta, \alpha^2\beta^2, \alpha\beta^3, \beta^4, \alpha^2r^2, \alpha\beta r^2, \beta^2r^2, r^4) + \dots \end{aligned} \quad (67)$$

where $(\delta p_{uv}^j)_r$, $(\delta p_{uv}^j)_{st}$ and $(\delta p_{uv}^j)_{q\zeta}$ are the changes caused by α_r , β_{st} and r_q , respectively, and are given by Eqs. 2, 7 and 12. The perturbed separate bond order by this orbital of the bond $(\eta\zeta)$ in another system, say, the system

$\Delta_i(\varepsilon)$, is

$$P_{\eta\zeta}^j = (\delta p_{\eta\zeta}^j)_{i\zeta} + C\{\alpha(r_i)^2, \beta(r_i)^2\} \\ + C\{\alpha^2(r_i)^2, \alpha\beta(r_i)^2, \beta^2(r_i)^2, r^2(r_i)^2\} + \dots \quad (68)$$

The perturbed k th orbital energy of a system, say, the system $\Delta_i(\varepsilon)$, is

$$\eta_{ik}' = \eta_{ik} + (\delta \eta_{ik})_{i\zeta} + C\{\alpha(r_i)^2, \beta(r_i)^2\} \\ + C\{\alpha^2(r_i)^2, \alpha\beta(r_i)^2, \beta^2(r_i)^2, r^2(r_i)^2\} + \dots \quad (69)$$

The perturbed separate bond orders by this orbital of bonds $(\eta\zeta)$ and (uv) are

$$P_{\eta\zeta}^{ik} = p_{\eta\zeta}^{ik} + (\delta p_{\eta\zeta}^{ik})_{i\zeta} + C\{\alpha(r_i)^2, \beta(r_i)^2\} \\ + C\{\alpha^2(r_i)^2, \alpha\beta(r_i)^2, \beta^2(r_i)^2, r^2(r_i)^2\} + \dots \quad (70)$$

$$P_{uv}^{ik} = (\delta p_{uv}^{ik})_{i\zeta} + C\{\alpha(r_i)^2, \beta(r_i)^2\} \\ + C\{\alpha^2(r_i)^2, \alpha\beta(r_i)^2, \beta^2(r_i)^2, r^2(r_i)^2\} + \dots \quad (71)$$

Also this bond order by this orbital of the bond $(\mu\nu)$, which is located in another system, say, the system $\Delta_k(\varepsilon)$, is given by

$$P_{\mu\nu}^{ik} = C\{(r_i)^2 (r_k)^2\} + \dots \quad (72)$$

The perturbed separate bond order of the bond which is made anew by perturbation between conjugated systems, say, the bond $(i\zeta)$ between the systems $\Delta(\varepsilon)$ and $\Delta_i(\varepsilon)$, may be written as

$$P_{i\zeta}^j = (\delta p_{i\zeta}^j)_{i\zeta} + C\{\alpha r_i, \beta r_i\} + C\{\alpha^2 r_i, \alpha\beta r_i, \beta^2 r_i, r^2 r_i\} \\ + C\{\alpha^3 r_i, \alpha^2\beta r_i, \alpha\beta^2 r_i, \beta^3 r_i, \alpha r^2 r_i, \beta r^2 r_i, \alpha(r_i)^3, \beta(r_i)^3\} + \dots \quad (73)$$

$$P_{1k}^{(k)} = (\delta p_{1k}^{(k)})_{1k} + C\{\alpha r_1, \beta r_1\} + C\{\alpha^2 r_1, \alpha \beta r_1, \beta^2 r_1, r_1^2 r_1\} \\ + C\{\alpha^3 r_1, \alpha^2 \beta r_1, \alpha \beta^2 r_1, \beta^3 r_1, \alpha r_1^2 r_1, \beta r_1^2 r_1, \alpha(r_1)^3, \beta(r_1)^3\} + \dots \quad (74)$$

$$P_{1k}^{(q)} = C\{\alpha(r_q)^2 r_1\} + C\{\alpha(r_q)^2 r_1, \beta(r_q)^2 r_1\} + \dots \quad (q = 2, 3, \dots, k) \quad (75)$$

As for the total π electronic energy an equation similar to Eq. 66, as for the total bond order (and the electron density) one similar to Eq. 67, and as for the total bond order of a newly formed bond one similar to Eq. 75 may be obtained.

Thus it has become clear to what order of perturbation terms the additivity rule applies, and what kinds of terms appear in several molecular quantities. If it is necessary, one could formulate cross terms in reference to the results of two perturbations.

§8. Degenerate Systems

In the previous sections it was assumed that no molecular orbital is degenerate with any other molecular orbital in the same molecule, not with molecular orbitals in any other system to be subjected to conjugation.

Even if some levels in the non-perturbed systems are degenerate, so far as they are chosen mutually orthogonal,

the perturbed orbital energy and the perturbed separate bond order (and electron density) corresponding to non-degenerate orbitals are not affected at all, that is, equations derived in the preceding section, giving separate quantities, are valid also in this case.

As for degenerate levels, on the other hand, the sum of the perturbed orbital energies or of the perturbed bond orders over all the degenerate levels is easily obtained by taking a limit of the corresponding sum which is derived as if they were not degenerate. For instance, in Case I, when the l th and the $(l+1)$ th levels are degenerate,

$$\begin{aligned} \varepsilon_l' + \varepsilon_{l+1}' &= \lim_{\varepsilon_{l+1} \rightarrow \varepsilon_l} [\varepsilon_l', \text{nondeg} + \varepsilon_{l+1}', \text{nondeg}] \\ &= 2\varepsilon_l + [\delta(\varepsilon_l + \varepsilon_{l+1})]_r + [\delta(\varepsilon_l + \varepsilon_{l+1})]_s \\ &\quad + 2 \sum_{(r, l, l+1)}^{\text{all}} \frac{C_r^k C_s^k (C_r^l C_s^l + C_r^{l+1} C_s^{l+1})}{\varepsilon_l - \varepsilon_k} (\alpha_r' \alpha_s') + \dots \end{aligned} \quad (76)$$

where

$$\begin{aligned} [\delta(\varepsilon_l + \varepsilon_{l+1})]_r &= [(C_r^l)^2 + (C_r^{l+1})^2] \alpha_r' \\ &\quad + \sum_{(r, l, l+1)}^{\text{all}} \frac{(C_r^k)^2 [(C_r^l)^2 + (C_r^{l+1})^2]}{\varepsilon_l - \varepsilon_k} (\alpha_r')^2 + \dots \end{aligned} \quad (77)$$

and $\varepsilon_l', \text{nondeg}$ is given by Eq. 27, which is derived for non-degenerate system. Explicit formulae for other various degenerate cases are omitted here for the sake of brevity,

but one might write them down without difficulty according to the above principle. The total π electronic energy and the bond order (or the electron density) being represented as the sums of orbital energies and separate orders (or densities) over the occupied orbitals, it is concluded that, even in the degenerate cases, if all the degenerate levels are occupied, the degeneracy does not affect the additivity rule, though concrete formulae involved may differ from the case of no degeneracy.

§9. Discussion

By the results obtained in the preceding sections the additivity rule concerning multiple perturbations and its limits of use have been clarified.

When a hetero-substitution of an atom in a conjugated system causes changes of the Coulomb integral of the atom and of the resonance integrals between neighboring atoms, their effects as a whole may be additively estimated in the first order perturbation treatment. When introduction of a conjugable group into a conjugated system as its certain atom gives rise simultaneously to a change of the Coulomb integral of the atom, the additivity rule applies to the first order terms.

Further, for the introduction of many substituents and hetero-substitutions, the additivity of these effects are materialized, and various examples are seen in experiments. The additivity of shift of absorption spectra would be explained by the additivity in the orbital energy. The vector additivity of dipole moment would be understood as the additivity in the electron density or in the amount of charge transfer. Aono and Higuchi⁴⁾ interpreted the additivity of hyperfine splitting in the electron spin resonance spectrum of substituted semiquinones in terms of the additivity in the unpaired electron density.

Speaking of reactivity indices, i.g. the frontier electron density, P_{uu}^f , localization energy, $\epsilon'(\text{localized state}) - \epsilon'(\text{non-localized state})$, total π electron density, P_{uu} , free valence, $\sqrt{3} - \sum_v P_{uv}$, and most other indices, the additivity rule is applicable to a certain order of perturbation terms. Superdelocalizability is also proved to fulfil the additivity rule.

If one practically evaluates the cross terms appearing in the formulae, one would be able to discuss the deviation from the additivity rule, which is also often realized in experiments.

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Chapter 3

Reactivity Indexes in SCF Method

§1. Introduction

In order to interpret chemical reactivity of conjugated molecules, there have been proposed several quantum-mechanical methods in LCAO MO treatment, such as the frontier electron method (frontier electron density and superdelocalizability as reactivity indexes)¹⁾, the static method (total π -electron density and self-polarizability for an ionic reaction and free valence for a radical reaction)²⁾, the localization method (localization energy)³⁾, and so on.

Within the scope of the simple LCAO MO treatment, where electronic interaction is not explicitly considered, total π -electron density of an alternant hydrocarbon is unity for all the positions⁴⁾, and accordingly in terms of the static method the ionic reactivity is to be determined by self-polarizability of each position. But once electronic interaction is taken into account, the uniformity of total π -electron distribution is immediately extinguished, so that its magnitude comes to correspond to the ionic reactivity in a molecule in the static method. For trans-butadiene the coefficients of AO's in MO's, calculated in semi-empirical

SCF method⁵⁾, in non-empirical SCF method⁶⁾ and in non-empirical SCF CI method⁷⁾, show the larger π -electron density, i.e., the larger electrophilic reactivity, at the position 2, contradictory to the experiments. Further, semi-empirical SCF calculation on naphthalene leads to an erroneous prediction of electrophilic reactivity⁸⁾.

For the purpose of obtaining more information on reactivity indexes, in the first two sections of the present chapter, we determine the coefficients of AO's in MO's of anthracene by semi-empirical LCAO SCF method. In the last section it is examined whether or not each of total π -electron density, free valence and frontier electron density remains a good index of chemical reactivity in SCF treatment.

§2. SCF Calculation on Anthracene

Roothaan has developed in detail the general formalism of LCAO SCF method for the closed configuration of a molecule⁹⁾. This will not be repeated here for the sake of brevity. Using his theory with only π -electrons considered explicitly, we numerically calculate the coefficients of AO's in SCF MO's of the ground state of anthracene.

The numbering of atoms and the co-ordinate of symmetry operation are shown in Fig. 1. The bond distances are taken

to be 1.370 Å for the bond 1-2, 1.396 Å for 9-11, 1.408 Å for 2-3, 1.423 Å for 1-11 and 1.436 Å for 11-12, and all the bond angles are assumed in a good approximation to be 120°¹⁰⁾.*

Necessary numerical evaluation of the resonance integrals, $\beta_{\mu\nu}$, and the Coulomb repulsion integral, $\gamma_{\mu\nu}$, is carried out on the semi-empirical formulae proposed by Pariser and Parr¹¹⁾. In the expression of the Coulomb integral, α_{μ} ,

$$\alpha_{\mu} = W_{2p} - \sum_{\nu(\neq \mu)} \{ \gamma_{\mu\nu} + (\nu : \mu\mu) \} \quad (1)$$

no particular values of the Coulomb penetration integral, $(\nu : \mu\mu)$, have been given by Pariser and Parr, and on the theoretical consideration¹²⁾ we have determined its average value as 0.85 eV. when the atoms μ and ν are adjacent, as 0.08 eV. when μ and ν are separated by a single atom, and as zero otherwise. W_{2p} in Eq. 1 is as usual the electronic energy of a carbon atom in its valence state and is regarded as a constant.

The obtained SCF MO's, ϕ_i , of the ground state of anthracene and their orbital energies, ϵ_i , are collected in Table I, together with un-occupied MO's.

* Deviations of all the observed bond angles from 120° are about 1-2°.

§3. SCF Reactivity Indexes and Discussion

First of all we define SCF frontier electron density in the same way as in simple LCAO treatment¹⁾, where the frontier orbital denotes the highest occupied one for an electrophilic reaction, the lowest unoccupied one for a nucleophilic reaction, and both for a radical reaction.

The calculated results of total π -electron density, free valence and frontier electron densities of anthracene are given in Table II. Values of these reactivity indexes in SCF method of naphthalene and trans-butadiene are collected in Tables III and IV, respectively.

Total π -electron density of anthracene is the largest at the position 11 and decreases in the order of 2, 1 and 9. The position 11 being out of the question because of its lack of hydrogen to be substituted, an electrophilic substitution should take place at the position 2 and a nucleophilic substitution at the position 9 on the basis of the static method. This prediction contradicts experimental results that the position 9 is the most reactive in an electrophilic substitution. Concerning naphthalene the position 2, where SCF total π -electron density has the largest value as shown in Table III, does not actually suffer from an electrophilic substitution. Furthermore, as for butadiene Table IV shows that total

π -electron densities by semi-empirical SCF method, by non-empirical SCF method and by non-empirical SCF CI method lead to the same erroneous prediction that the position 2 is the most susceptible to an electrophilic reaction. Thus SCF total π -electron density is no longer a good index for chemical reactivity.

On the contrary, it will be valuable to emphasize that SCF frontier electron density correctly predicts the most reactive positions, that is, the position 9 in anthracene, 1 in naphthalene and 1 in butadiene for all the three kinds of reactions. It may be, therefore, concluded that frontier electron density remains a good reactivity index even when the electronic interaction is explicitly included.

So far as our approximation is concerned, free valence seems to give correct results in the three hydrocarbons, as shown in Tables II, III and IV. In comparison with this, we have collected in Table V values of free valence of some hydrocarbons, which have been derived from the SCF bond orders obtained by Pritchard and Sumner¹³). It can be seen in Table V that this free valence leads to a seriously erroneous conclusion for anthracene and for pyrene: anthracene is, as is well known, the most susceptible to a radical attack at the position 9, and pyrene is so at 1. On inspection of these

and other results of SCF calculation¹⁵⁾, it may be said that the value of bond order, or that of free valence, varies very easily depending on the degree of approximation employed and on the semi-empirical method of evaluating atomic integrals. Such an unstable quantity would probably not deserve a reliable reactivity index.

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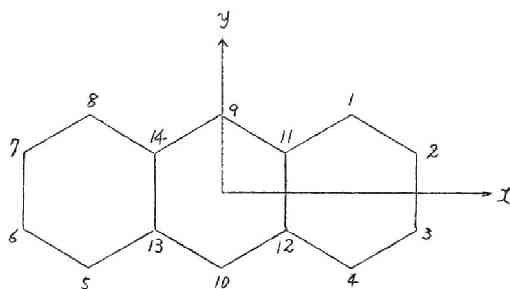


Fig. 1. The numbering of atoms and the coordinate of symmetry operation of anthracene.

Table I. SCF MO'S and Their Orbital Energies of Anthracene

Symmetry Orbital energy ³⁾		MO		occupied
b_{1u}	$\varepsilon_1 = -5.762$	$\psi_1 = 0.4887\sigma_4$	$+ 0.4448\sigma_5$	$+ 0.3323\sigma_6 + 0.6730\sigma_7$
b_{2g}	$\varepsilon_2 = -5.190$	$\psi_2 = 0.5818\sigma_8$	$+ 0.6276\sigma_9$	$+ 0.5174\sigma_{10}$
b_{1u}	$\varepsilon_3 = -3.350$	$\psi_3 = 0.3108\sigma_4$	$+ 0.7098\sigma_5$	$- 0.3717\sigma_6 - 0.5113\sigma_7$
b_{3g}	$\varepsilon_4 = -3.196$	$\psi_4 = 0.6278\sigma_6$	$+ 0.3465\sigma_{12}$	$+ 0.4423\sigma_{13} + 0.5386\sigma_{14}$
a_{1u}	$\varepsilon_5 = -2.433$	$\psi_5 = 0.7932\sigma_1$	$+ 0.4861\sigma_2$	$+ 0.3668\sigma_3$
b_{2g}	$\varepsilon_6 = -1.9935$	$\psi_6 = 0.0792\sigma_8$	$+ 0.5894\sigma_9$	$- 0.8039\sigma_{10}$
b_{3g}	$\varepsilon_7 = -0.2930$	$\psi_7 = 0.5130\sigma_{11}$	$+ 0.4221\sigma_{12}$	$- 0.6793\sigma_{13} - 0.3177\sigma_{14}$
b_{1u}	$\varepsilon_8 = +7.1369$	$\psi_8 = 0.4431\sigma_4$	$- 0.3746\sigma_5$	$- 0.7573\sigma_6 + 0.2997\sigma_7$
a_{1u}	$\varepsilon_9 = +7.6451$	$\psi_9 = 0.0811\sigma_1$	$+ 0.5125\sigma_2$	$- 0.8548\sigma_3$
b_{2g}	$\varepsilon_{10} = +9.124$	$\psi_{10} = 0.8095\sigma_8$	$- 0.5087\sigma_9$	$- 0.2932\sigma_{10}$
b_{1u}	$\varepsilon_{11} = +9.668$	$\psi_{11} = 0.6843\sigma_4$	$- 0.3974\sigma_5$	$+ 0.4219\sigma_6 - 0.4425\sigma_7$
b_{3g}	$\varepsilon_{12} = +9.726$	$\psi_{12} = 0.1781\sigma_{11}$	$- 0.5967\sigma_{12}$	$- 0.5090\sigma_{13} + 0.5943\sigma_{14}$
a_{1u}	$\varepsilon_{13} = +11.747$	$\psi_{13} = 0.6035\sigma_1$	$- 0.7079\sigma_2$	$- 0.3671\sigma_3$
b_{3g}	$\varepsilon_{14} = +12.069$	$\psi_{14} = 0.5576\sigma_{11}$	$- 0.5880\sigma_{12}$	$+ 0.2895\sigma_{13} - 0.5095\sigma_{14}$

where b) $\sigma_1 = (1/2)(\phi_1 - \phi_4 + \phi_5 - \phi_8)$, $\sigma_2 = (1/2)(\phi_2 - \phi_5 + \phi_8 - \phi_{11})$, $\sigma_3 = (1/2)(\phi_1 - \phi_2 + \phi_3 - \phi_4)$, $\sigma_4 = (1/2)(\phi_1 + \phi_4 + \phi_5 + \phi_8)$, $\sigma_5 = (1/2)(\phi_2 + \phi_5 + \phi_8 + \phi_{11})$, $\sigma_6 = (1/\sqrt{2})(\phi_9 + \phi_{10})$, $\sigma_7 = (1/2)(\phi_{11} + \phi_{12} + \phi_{13} + \phi_{14})$, $\sigma_8 = (1/2)(\phi_1 + \phi_4 - \phi_5 - \phi_8)$, $\sigma_9 = (1/2)(\phi_2 + \phi_5 - \phi_8 - \phi_{11})$, $\sigma_{10} = (1/2)(\phi_{11} + \phi_{12} - \phi_{13} - \phi_{14})$, $\sigma_{11} = (1/2)(\phi_1 - \phi_4 - \phi_5 + \phi_8)$, $\sigma_{12} = (1/2)(\phi_2 - \phi_5 - \phi_8 + \phi_{11})$, $\sigma_{13} = (1/\sqrt{2})(\phi_9 - \phi_{10})$, $\sigma_{14} = (1/2)(\phi_{11} - \phi_{12} - \phi_{13} + \phi_{14})$

a) W_{xp} as standard. In units of eV. b) ϕ_i is the AO on the i -th atom.

Table II. Values of SCF Reactivity Indexes of Anthracene

Position	Total π -electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
1	0.983	0.459	0.132	0.098	0.115
2	0.989	0.443	0.089	0.070	0.080
9	0.906	0.511	0.461	0.574	0.517
11	1.075	0.130	0.049	0.045	0.047

Table III. Values of SCF Reactivity Indexes of Naphthalene^{a)}

Position	Total π -electron density	Free valence	Fontier electron density		
			Electrophilic	Nucleophilic	Radical
1	0.967	0.453	0.334	0.339	0.343
2	1.003	0.435	0.166	0.162	0.157
9	1.062	0.158	0	0	0

a) Ref. 8.

Table IV. Values of SCF Reactivity Indexes of trans-Butadiene

-45-

Position	Total π -electron density	Free valence	Frontier electron density		
			Electrophilic	Nucleophilic	Radical
A) Semi-empirical SCF method ^{a)}					
1	0.938	0.757	0.575	0.606	0.637
2	1.062	0.545	0.425	0.394	0.363
B) Non-empirical SCF method ^{b)}					
1	0.975	---	0.620	0.633	0.645
2	1.025	---	0.380	0.367	0.355
C) Non-empirical SCF CI method ^{c)}					
1	0.978	---	---	---	---
2	1.022	---	---	---	---
a) Ref. 5.		b) Ref. 6.	c) Ref. 7.		

Table V. Values of SCF Free Valence of Hydrocarbons
in Rougher Approximation^{a)}

Molecule	Position	Free valence
Naphthalene	1	0.447
	2	0.420
Anthracene	1	0.473
	2	0.441
	9	0.468
Phenanthrene	1	0.431
	2	0.408
	3	0.409
	4	0.428
	9	0.474
Chrysene	1	0.461
	2	0.464
	3	0.439
	4	0.434
	5	0.435
	6	0.436
Pyrene	1	0.432
	2	0.395
	4	0.485

a) Ref. 13.*

* Their assumptions are the same as those that are presented by Pople¹⁴⁾, the main points of which are (1) neglect of the Coulomb penetration integral, and (2) assumption of equi-bond-length and of regular hexagone of carbon ring, and (3) that the Coulomb repulsion integral, $V_{\mu\nu}$, is expressed in the following form.

$$V_{\mu\nu} = e^2/R_{\mu\nu} \quad (R_{\mu\nu} : \text{distance between the atoms } \mu \text{ and } \nu)$$

Chapter 4

Localization Energy with Electronic Interaction

§1. Introduction

The localization method by Wheland¹⁾, in which localization energy is employed as the reactivity index, has achieved successes in interpreting chemical reactivity of conjugated molecules²⁾. On the other hand, total π -electron density³⁾, self-polarizability⁴⁾, free valence⁵⁾, frontier electron density⁶⁾ and superdelocalizability⁷⁾ are introduced as good reactivity indexes in the approximation of the simple LCAO treatment. Regarding alternant hydrocarbons (AH's) some mathematical relations have been found between localization energy and other reactivity indexes⁸⁾.

In the previous chapter, utilizing LCAO SCF wave function where electronic interaction is explicitly included, we have found that the total π -electron density can not predict the correct reactivity of molecules, while the frontier electron density remains a good index for both ionic and radical reactions in LCAO SCF MO treatment just as well as in usual simple LCAO MO treatment.⁹⁾ In the present chapter, we have defined and calculated the localization energy under an explicit consideration of electronic

interaction, and comparison of the results obtained by the present method with those in simple LCAO treatment has been made.

§2. Model of Localized Systems

According to Wheland's definition the localized system in the transition state has the configuration in which the attacked carbon atom is sp^3 -hybridized, so that the resonance integrals between the attacked atom and the neighboring ones are taken to be zero. More precisely the integral does not completely vanish; however, in order to be faithful to the concept of the term "localization", we assume that the resonance integrals between the attacked atom and the others are always zero. This assumption may be reasonable for our approximate calculation.

Here one more problem arises: Simple treatment naturally allows us to deal with the two parts, the localized electrons and the residue, independently from each other; but when we want to take the electronic interaction into account, the interaction between the two parts, and that between those two and the attacking reagent must be considered, as well as the mutual interaction of electrons inside the residue*.

* In electrophilic reaction, the interaction between the two localized electrons is also to be included.

where ψ_i is the i -th MO, α and β are the spin functions, and the superscripts denote the numbering of electrons. Each MO should be chosen to minimize the electron energy of the system; but so far as the evaluation of localization energy with electronic interaction is concerned, it seems sufficient to use Huckel MO

$$\phi_i = \sum_{\mu} c_{i\mu} \phi_{\mu} \quad (i = 1, 2, \dots, 2n) \quad (2)$$

where ϕ_{μ} denotes the AO on the μ -th carbon atom.

Introducing a SCF-like procedure proposed by Pople¹⁰), we obtain the following expression of the total electronic energy of the system *.

$$\begin{aligned} \varepsilon_0 = & 2nU + (\gamma_{\mu\mu}/4) \sum_{\mu} (P_{\mu\mu})^2 + 2\beta \sum_{\mu < \nu}^* P_{\mu\nu} \\ & + \sum_{\mu < \nu} \{ (P_{\mu\mu} - 1)(P_{\nu\nu} - 1) - (1/2)(P_{\mu\nu})^2 \} \gamma_{\mu\nu} \end{aligned} \quad (3)$$

where U is a core matrix element and is put a constant,

β is the resonance integral between the nearest neighbors,

and $\gamma_{\mu\nu}$ is the Coulomb repulsion integral

$$\gamma_{\mu\nu} = \int \phi_{\mu}^*(1) \phi_{\nu}^*(2) \frac{e^2}{\gamma_{12}} \phi_{\mu}(1) \phi_{\nu}(2) dv_1 dv_2 \quad (4)$$

and

$$P_{\mu\nu} = 2 \sum_{i=1}^n c_{i\mu} c_{i\nu} \quad (5)$$

* Core-core repulsion energies are included in all the expressions of energies in this paper.

Summation Σ and Σ^* should cover all the atoms and the nearest neighboring atoms, respectively. In deriving Eq. 3 the same assumptions as proposed by Pople¹⁰⁾, for instance, of equi-bond-length, of neglecting the Coulomb penetration integrals and so on, are employed.

From the assumption made in the preceding section the wave function χ_E of the "localized" system (transition complex) for electrophilic reaction, in which two electrons are localized on the carbon λ , may be written as follows:

$$\begin{aligned} \chi_E = & (1/\sqrt{(2n-2)!}) [(\psi'_1, \alpha)(\psi'_1, \beta)^2 \dots \dots \\ & \times (\psi'_{n-1}, \alpha)(\psi'_{n-1}, \beta)^{2n-2}] \\ & \times (1/\sqrt{2!}) [(\phi_\lambda \alpha)^{2n-1}(\phi_\lambda \beta)^{2n}] \end{aligned} \quad (6)$$

where ψ'_i is the i -th Hückel MO for the residue consisting of $(2n-1)$ carbons.

$$\psi'_i = \sum_{\mu} c'_{i\mu} \phi_{\mu} \quad (i = 1, 2, \dots, 2n-1) \quad (7)$$

Here we refer the superscript "1" to the residue of the molecule. The two parts being treated separately (Approx. 1), the energy of the system, ε_{E0} , is given as follows¹¹⁾:

$$\begin{aligned}
\varepsilon_{E0} = & 2U + \gamma_{\mu\mu} + (2n-2)U + (\gamma_{\mu\mu}/4) \sum_{\mu} (P_{\mu\mu}^+)^2 \\
& + 2\beta \sum_{\mu < \nu}^* P_{\mu\nu}^+ + \sum_{\mu < \nu} \{ (P_{\mu\mu}^+ - 1)(P_{\nu\nu}^+ - 1) \\
& - (1/2)(P_{\mu\nu}^+)^2 \} \gamma_{\mu\nu}
\end{aligned} \tag{8}$$

where

$$P_{\mu\nu}^+ = 2 \sum_{i=1}^{n-1} c'_{i\mu} c'_{i\nu} \tag{9}$$

The first two terms correspond to the energy of the localized electrons and the others to that of the residue. When the interaction between the parts is taken into account in higher approximation (Approx. 2), the interaction energy ε_{E1} :

$$\varepsilon_{E1} = \sum_{\mu} (P_{\mu\mu}^+ - 1) \gamma_{\mu\mu} \tag{10}$$

is to be added to the energy ε_{E0} .

Also for nucleophilic reaction, through the similar consideration as for electrophilic one, we easily obtain the following formulae.

$$\begin{aligned}
\chi_N = & (1/\sqrt{(2\pi)^I}) [(\psi'_{1\alpha})^I (\psi'_{1\beta})^2 \dots \dots \\
& \times (\psi'_{n\alpha})^{2n-1} (\psi'_{n\beta})^{2n}]
\end{aligned} \tag{11}$$

$$\begin{aligned}
\varepsilon_{N0} = & 2nU + (\gamma_{\mu\mu}/4) \sum_{\mu} (P_{\mu\mu}^-)^2 \\
& + 2\beta \sum_{\mu < \nu}^* P_{\mu\nu}^- + \sum_{\mu < \nu} \{ (P_{\mu\mu}^- - 1) \\
& \times (P_{\nu\nu}^- - 1) - (1/2)(P_{\mu\nu}^-)^2 \} \gamma_{\mu\nu}
\end{aligned} \tag{12}$$

$$\varepsilon_{N1} = \sum_{\mu} (1 - P^{-}_{\mu\mu}) \gamma_{\mu\lambda} \quad (13)$$

$$P^{-}_{\mu\nu} = 2 \sum_{i=1}^n C'_{i\mu} C'_{i\nu} \quad (14)$$

For radical reaction,

$$\begin{aligned} \chi_R = & (1/\sqrt{(2n-1)!}) [(\psi', \alpha)^i (\psi', \beta)^2 \dots \\ & \times (\psi'_{n-1}, \alpha)^{2n-3} (\psi'_{n-1}, \beta)^{2n-2} \\ & \times (\psi'_{n\alpha})^{2n-1}] \cdot (\phi_{\lambda\alpha})^{2n} \end{aligned} \quad (15)$$

$$\begin{aligned} \varepsilon_{R0} = & U + (2n-1)U + \gamma_{\mu\mu} \sum_{\mu} P^{\alpha}_{\mu\mu} P^{\beta}_{\mu\mu} \\ & + 2\beta \sum_{\mu < \nu}^* P^{\alpha}_{\mu\nu} + \sum_{\mu < \nu} \{ (P^{\alpha}_{\mu\mu} - 1)(P^{\alpha}_{\nu\nu} - 1) \\ & - [(P^{\alpha}_{\mu\nu})^2 + (P^{\beta}_{\mu\nu})^2] \} \gamma_{\mu\nu} \end{aligned} \quad (16)$$

$$\varepsilon_{R1} = 0 \quad (17)$$

$$\left. \begin{aligned} P^{\alpha}_{\mu\nu} &= \sum_{i=1}^n C'_{i\mu} C'_{i\nu} = (1/2) P^{-}_{\mu\nu} \\ P^{\beta}_{\mu\nu} &= \sum_{i=1}^{n-1} C'_{i\mu} C'_{i\nu} = (1/2) P^{+}_{\mu\nu} \\ P^0_{\mu\nu} &= P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu} \end{aligned} \right\} \quad (18)$$

The first term in Eq. 16 refers to the localized electron and the others to the residue.

As regards the AH, whose MO has special simplifying properties, Eqs. 8, 10, 12, 13 and 16 can be reduced to

simpler ones, that is,

$$\begin{aligned}
 E_{N0} = & \varepsilon_{E0} \, 2nU + (\gamma_{\mu\mu}/4) [(n-1) \\
 & + \sum_{\mu\nu}^{st} \{1 + (c'_{n\mu})^2\}^2] + 2\beta \sum_{\mu<\nu}^* P_{\mu\nu}^0 \\
 & - \{ - \sum_{\mu<\nu}^{st,st} (c'_{n\mu} c'_{n\nu})^2 + \sum_{\mu',\nu}^{st,unst} (P_{\mu\nu}^0)^2 \} (\gamma_{\mu\nu}/2)
 \end{aligned} \tag{19}$$

$$\varepsilon_{N1} = \varepsilon_{E1} = - \sum_{\mu}^{st} (c'_{n\mu})^2 \gamma_{\mu\lambda} \tag{20}$$

$$\begin{aligned}
 E_{R0} = & 2nU + (\gamma_{\mu\mu}/4) \{ (2n-1) - \sum_{\mu}^{st} (c'_{n\mu})^4 \} \\
 & + 2\beta \sum_{\mu<\nu}^* P_{\mu\nu}^0 - \{ \sum_{\mu<\nu}^{st,st} (c'_{n\mu} c'_{n\nu})^2 \\
 & + \sum_{\mu,\nu}^{st,unst} (P_{\mu\nu}^0)^2 \} (\gamma_{\mu\nu}/2)
 \end{aligned} \tag{21}$$

Summation \sum^{st} and \sum^{unst} should cover all the starred and the unstarred atoms, respectively.

The localization energies, L , of the λ -th carbon atom are, therefore, obtained from the following equations.

Electrophilic Reaction

$$(\text{Approx. 1}) \quad L_E = \varepsilon_{E0} - \varepsilon_0$$

$$(\text{Approx. 2}) \quad L_E = \varepsilon_{E0} + \varepsilon_{E1} - \varepsilon_0$$

Nucleophilic Reaction

$$(\text{Approx. 1}) \quad L_N = \varepsilon_{N0} - \varepsilon_0$$

$$(\text{Approx. 2}) \quad L_N = \varepsilon_{N0} + \varepsilon_{N1} - \varepsilon_0$$

Radical Reaction

$$(\text{Approxs. 1 \& 2}) \quad L_R = \varepsilon_{R0} + \varepsilon_0$$

(22)

It is easily proved that the following wave functions χ'_E and χ'_R , instead of Eqs. 6 and 15, directly lead to the same energy expressions that were derived in Approx. 2, ε'_E and ε'_R respectively.

$$\chi'_E = (1/\sqrt{(2n)!}) [(\psi'_1\alpha)'(\psi'_1\beta)^2 \dots (\psi'_{n-1}\alpha)^{2n-3} \times (\psi'_{n-1}\beta)^{2n-2} (\phi_\lambda\alpha)^{2n-1} (\phi_\lambda\beta)^{2n}] \quad (23)$$

$$\varepsilon'_E = \varepsilon_{E0} + \varepsilon_{E1} \quad (24)$$

$$\begin{aligned} \chi'_R = & (1/\sqrt{(2n)!}) [(\psi'_1\alpha)'(\psi'_1\beta)^2 \dots (\psi'_{n-1}\alpha)^{2n-3} \\ & \times (\psi'_{n-1}\beta)^{2n-2} (1/\sqrt{2}) \\ & \times \{(\psi'_n\alpha)^{2n-1} (\phi_\lambda\beta)^{2n} \\ & - (\psi'_n\beta)^{2n-1} (\phi_\lambda\alpha)^{2n}\}] \end{aligned} \quad (25)$$

$$\varepsilon'_R = \varepsilon_{R0} \quad (26)$$

For numerical evaluation of β and $\gamma_{\mu\nu}$ are utilized the semi-empirical formulae introduced by Pariser and Parr¹²⁾. For simplicity, as partly stated above, all the C-C bond distances are assumed the same, 1.39Å, and all the carbon rings (five- and seven-membered rings for azulene and fulvalene, six-membered rings for the other molecules now considered) are supposed to be regular, and polyenyl bond angles to be 120°.

§4. Results and Discussion

The calculated results of localization energy, which is defined in the preceding section, of seven AH's and two non-AH's are listed in Tables I and II***, together with those obtained by simple LCAO treatment.

As is seen from Eq. 20, the interaction energy between the localized electrons and the residue in nucleophilic and in electrophilic reactions is necessarily negative for the AH, namely, there rises some stabilization of the system from the interaction, this seeming true also for the non-AH (cf. Eqs. 10 and 13); and accordingly the values of the localization energies, χ_E and χ_N , in Approx. 1 are larger than in Approx. 2. For all that we can see in Table I and II that in both approximations we obtain nearly the same

*** For the position 2 of butadiene, the wave functions of the localized system are expressed in the product of wave functions of three parts, as follows:

$$\begin{aligned}\chi_E &= (1/\sqrt{2}) [(\phi_1'\alpha)'(\phi_1'\beta)^2] \\ &\quad \times (1/\sqrt{2}) [(\phi_2\alpha)^3(\phi_2\beta)^4] \\ \chi_R &= (1/\sqrt{2}) [(\phi_1'\alpha)'(\phi_1'\beta)^2] \cdot (\phi_2\alpha)^3 \cdot (\phi_1\alpha)^4 \\ \chi_N &= (1/\sqrt{2}) [(\phi_1'\alpha)'(\phi_1'\beta)^4] \\ &\quad \times (1/\sqrt{2}) [(\phi_1\alpha)^3(\phi_1\beta)^4]\end{aligned}$$

In Approx. 1 three parts are treated independently, whereas their mutual interactions are taken into account in Approx. 2.

intramolecular orientation, which will be discussed in the later paragraph in detail. In radical reaction, on the other hand, the interaction energy formally vanishes (cf. Eq. 17), and therefore both approximations give the same value of localization energy.

It will be seen in Tables I and II that the magnitude of L_R is generally much smaller than those of L_N and L_E in both approximations, whereas in the simple LCAO treatment the magnitude of L_R lies between those of L_N and L_E . This by no means admits that the activation energy of radical reaction is smaller than those of the others, because effects of reagents and changes in the σ -system are conventionally set aside from this argument. Especially for the AH Eqs. 19 and 20 show the relation $L_E = L_N$ within each approximation in accordance with the result obtained by the simple treatment.

It may be valuable to notice that both approximations indicate the same intramolecular orientation as the simple treatment for all the reactions of the molecules now concerned, except for the ionic reactions of phenanthrene in Approx. 1. Accordingly, its agreement with experimental results is mostly good, but the facts that azulene reacts at the position 1 in radical reaction¹³⁾ (L_R is the smallest

at 4) and that the position 4 of biphenyl is more reactive than the position 2 both in radical and electrophilic reactions¹⁴⁾ (L_R and L_E indicate 2-orientation) can not be explained on the basis of the localization energy, whether the electronic interaction is taken into account or not. In fulvalene the position 1 is shown to be the most susceptible to attack by localization energies and the position 2 is so by frontier electron density¹⁵⁾, superdelocalizability¹⁵⁾ and total π -electron density¹⁶⁾, further experiments being awaited at this point.

It seems also interesting that, except for the mutual coincidence of the most reactive position, the order of reactivity of each position in azulene does not coincide with one another in the three treatments; in electrophilic reaction, for instance, the reactivity of each position decreases in the order $1 > 5 > 2 > 4 > 6$ in the simple treatment, $1 > 2 > 5 > 6 > 4$ in Approx. 1, and $1 > 5 > 6 > 2 > 4$ in Approx. 2.

As it is seen in Fig. 1, agreement of the intermolecular order of reactivity predicted by the simple treatment with that obtained with electronic interaction is not so good in Approx. 2; and in Approx. 1 the agreement is a little worse. Non-AH's, azulene and fulvalene, largely deviate from the

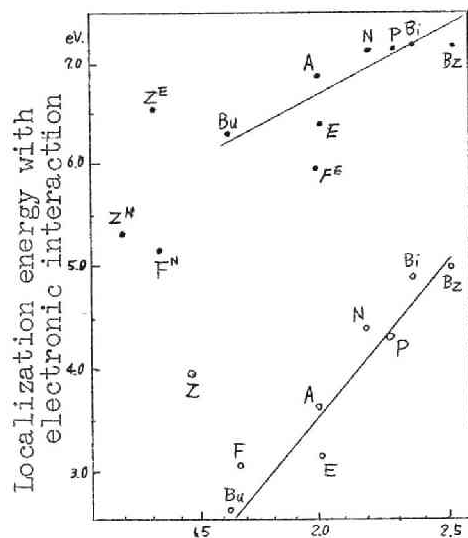
linear relationship of Fig. 1, but unfortunately there are no available data to check which result is correct.

From the above discussion it might be concluded that the localization energy, in which the electronic interaction is taken into account, can be a pretty good index of chemical reactivity.

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Localization energy in simple treatment ($-\mathcal{S}$)

Fig. 1. Relationship between localization energies in simple treatment and with electronic interaction.

O : Radical reaction, ● : Ionic reaction

(Approx. 2); E: ethylene, Bu: butadiene, Bz: benzene,

N: naphthalene, A: anthracene, P: phenanthrene,

F: fulvalene (F^N: nucleophilic, F^E: electrophilic),

Z: azulene (Z^N: nucleophilic, Z^E: electrophilic).

Only the position of the smallest localization energy of each molecule is plotted. The straight lines are only for AH's.

Table I. Localization Energies of Alternant Hydrocarbons

Compound	Position	Ionic ($L_N=L_E$) ^{a)}		Radical (L_R) ^{a)} Approxs. 1 & 2	Simple ^{b)} ($L_N=L_E=L_R$)
		Approx. 1	Approx. 2		
Ethylene	--	13.695	6.395	3.165	2.000
Butadiene (trans)	1	11.854	6.324	2.590	1.694
	2	14.467	7.167	3.937	2.472
Benzene	--	13.834	7.334	4.995	2.536
Naphthalene	1	12.918	7.134	4.411	2.299
	2	13.470	7.473	4.888	2.480
Anthracene	1	12.575	7.160	4.255	2.240
	2	13.233	7.676	4.755	2.423
	9	11.806	6.882	3.636	2.013
Phenanthrene	1	12.821	7.212	4.604	2.317
	9	12.872	7.147	4.361	2.297
Biphenyl	2	13.157	7.191	4.905	2.400
	4	13.196	7.483	4.944	2.447

a) In units of eV .

b) In units of $(-\beta)$.

b) In units of $(-\beta)$.

Table II. Localization Energies of Non-Alternant Hydrocarbons

Compound	Position	Electrophilic(L_E)			Nucleophilic(L_N)			Radical(L_R)	
		Approx. 1a)	Approx. 2a)	Simple ^{b)}	Approx. 1a)	Approx. 2a)	Simple ^{b)}	Approx. 1 & 2a)	Simple ^{b)}
Azulene	1	11.392	6.543	1.352	13.265	7.572	2.090	4.177	1.721
	2	12.521	8.100	1.728	12.734	6.694	1.728	4.500	1.728
	4	13.760	8.148	1.808	10.559	5.280	1.231	3.987	1.520
	5	12.654	6.655	1.659	12.595	8.274	1.655	4.485	1.655
	6	13.755	7.349	1.959	11.177	8.959	1.280	4.368	1.620
Fulvalene	1	12.908	5.969	1.987	9.408	5.145	1.365	3.021	1.676
	2	13.702	6.680	2.236	10.507	7.131	1.452	3.783	1.848

a) In units of eV .

b) In units of $(-\beta)$.

Chapter 5

Frontier Electron Theory and Z Value

§1. Introduction

For all the MO (molecular-orbital) theoretical contributions which have been made on the chemical reactivity of conjugated molecules, there remains much to be revealed on the essential feature of aromatic substitution or of other reactions of conjugated molecules.

A theory of chemical reactivity of conjugated molecules, called the "frontier electron theory," has been presented by Fukui et al.¹⁾ In that theory the highest occupied and the lowest unoccupied MO's in the ground state played a dominant role. In other words, the intramolecular orientation could well be predicted by the density distribution of the electrons occupying these particular orbitals. The discovery of the peculiar behavior of these electrons (frontier electrons) may thus be said to have afforded materials which might be a clue to elucidating the mechanism of aromatic substitution. Nagakura and Tanaka²⁾ concluded from experimental data that an electrophilic substitution takes place only when the lowest unoccupied level of the attacking reagent is of lower energy than the highest

occupied one of the substrate and that a nucleophilic reaction occurs only when the lowest unoccupied level of the substrate lies energetically lower than the highest occupied level of the nucleophilic reagent. (This condition will hereafter be called condition A.) On the other hand Fukui et al. proposed a mechanism of aromatic substitution which involves a charge transfer through a hyperconjugation between the substrate and the reagent. In this mechanism the approaching reagent and the leaving atom were treated as the constituents of a pseudoatom having a π -type orbital (quasi- π orbital). By adopting this mechanism the characteristic behavior of frontier electrons was successfully explained, and a reactivity index, superdelocalizability, which is applicable to predicting the intermolecular relative reactivity, was simultaneously derived.³⁾ Further, in the latest paper,⁴⁾ the mechanism of charge transfer, as previously mentioned, was investigated more minutely. The theoretical conclusions are summarized as follows:

1. In order that an electrophilic, or a nucleophilic, substitution can occur, the energy of reagents must satisfy condition A. But it is to be noted that the meaning of the orbital energies is somewhat different from that of Nagakura and Tanaka. They settled condition A on the basis of the ionization potential and the electron affinity, in principle,

of the reagent having been submitted to the transfer of one electron, whereas we meant the Coulomb integral of the orbital, which will participate in the bond formation, of the reagent without charge transfer.

2. The energy of the quasi- π orbital in an electrophilic, or a nucleophilic, substitution rises or falls swiftly to the height of a frontier orbital instantaneously with hyperconjugation and then increases or decreases continuously with increasing extent of hyperconjugation to the transition state, where it will be near the Coulomb integral of a carbon atom.

3. Frontier electron density, superdelocalizability, and a generalized index are derived as reactivity indexes from the hyperconjugation energy at the transition state.

Recently, another theoretical contribution to the mechanism of electrophilic substitution has been presented by Brown.⁵⁾ At the transition state of the rate-determining step in some electrophilic substitutions of aromatic hydrocarbons, he thought, a complex is formed between the substrate and the reagent because of a charge transfer through the position of substitution, and that thus the stabilization energy of the complex is the most important factor affecting the reactivity. After condition A concerning energy levels

of the substrate and the reagent, he treated this complex quantum-chemically as an intermediate between the configuration without charge transfer and the configurations corresponding to the transfer of one electron from occupied orbitals of the substrate to the unoccupied orbital of the electrophile, that is, in a simple form of configuration interaction treatment of the charge-transfer complex discussed by Mulliken.⁶⁾ Thus he concluded that a quantity, what he called the "Z value," which refers only to the frontier orbital of the substrate would be an index of reactivity.

In this chapter, mathematical interrelations between the superdelocalizability and the Z value are pointed out both in heterolytic and homolytic reactions. A few comparative discussions on the theories of the mechanism of aromatic substitution are also made.

§2. Mathematical Interrelations between Superdelocalizability and Z Value-----

1. Heterolytic Reaction

First of all the electrophilic reaction will be considered. Suppose $e_E (= \alpha + \lambda \beta)$ and $e_f (= \alpha + \lambda_f \beta)$ are the energy of the unoccupied orbital of the electrophile and that of the frontier orbital for an electrophilic attack

(the highest occupied orbital) of the substrate, respectively where α and β are the Coulomb integral of a carbon atom and the resonance integral of a benzene bond, then condition A is written as

$$e_f - e_E = (-\beta)(h - \lambda_f) = (-\beta)Y_f > 0. \quad (1)$$

Since $(-\beta)$ is positive, Y_f must be positive.

It would now be desirable to summarize the procedures and results given by Brown.⁵⁾ It was proved that the stabilization energy due to the contribution of all possible charge-transfer configurations is expressed in units of $(-\beta)$ by the largest root (Z_0) of the following equation:

$$F(Z) = Z - \sum_i^{\infty} [2(C_r^i)^2 \gamma^2 / (Z - Y_i)] = 0, \quad (2)$$

where C_r^i is the coefficient of the r th atomic orbital (χ_r) in the i th MO whose energy is $\alpha + \lambda_i \beta$, Y_i is equal to $(h - \lambda_i)$, γ is a positive quantity which represents the extent of interaction between the r th atomic orbital and the electrophile at the transition state, and \sum_i^{∞} should cover all occupied MO's. For small γ , after utilizing a perturbation theory and neglecting higher orders of γ , Z_0 is directly obtained from Eq. 2, as follows:

$$Z_0 = Y_f + [2(C_r^f)^2 \gamma^2 / Y_f]. \quad (3)$$

(the larger its magnitude, the more reactive that position).

Brown adopted Z_0 , calling it the Z value, as a reactivity index for the electrophilic substitution, and by adjusting the values of h and γ succeeded in interpreting the rate of nitration of conjugated hydrocarbons. It is very interesting that in his theory the frontier orbital plays an exclusive role in deciding not only the intramolecular orientation but the intermolecular relative reactivity. In this sense his theory may serve as an alternate physical basis of the frontier electron theory. But on this point some discussions are to be given in the last section.

We might add a few remarks on his procedure with respect to the following points:

1. Figure 1 illustrates two relations $y = f(Z)$ and $y = Z$, where

$$f(Z) = \sum_i^{\text{occ}} [2(C_r^i)^2 \gamma^2 / (Z - Y_i)] \quad (4)$$

Of the values of Z at interseecting points of the two relations the largest one corresponds to Z_0 . This figure will be useful later for comparing with the case where Y_f is negative.

2. In Brown's paper⁵⁾ it seems as if Eq. 3 resulted

from deliberately taking only two configurations (one without charge transfer and one with charge transfer from the frontier orbital to the electrophile) into account from all possible configurations and then regarding γ small. It is of importance to notice that the more general Eq. 2, which includes all configurations, leads directly to Eq. 3, provided γ is small enough.

Now from the point of view of the quasi- π orbitals used in our previous theoretical studies, the configuration interaction treatment of the mechanism of an electrophilic substitution will be given.

According to our theory the energy of the quasi- π orbital gets and stays higher than that of the highest occupied orbital of the substrate at the transition state. If we again put the energy of the quasi- π orbital $\alpha + h\beta$, γ_f is negative in this case. These mathematical circumstances are essentially different from Brown's theory. Equation 2 is valid also in this case; but, as illustrated in Fig. 2, the largest root is never given by Eq. 3. It is easily expanded with respect to γ and, neglecting higher terms of γ , is written:

$$Z_0 = \sum_i^{occ} [2(C_i^1)^2 / (-\gamma_i)] \gamma^2 = \sum_i^{occ} [2(C_i^1)^2 / (\lambda_i - h)] \gamma^2. \quad (5)$$

This is the same as that previously obtained by Fukui et al. 4(b) a generalized form of the superdelocalizability. As an extreme case, when the adjustable parameter h is taken as zero, Eq. 5 becomes simply

$$Z_0 = \sum_i^{occ} [2(C_i^i)^2 / \lambda_i] \gamma^2 \equiv S_r^{(E)} \gamma^2, \quad (6)$$

where $S_r^{(E)}$ is the superdelocalizability for an electrophilic attack.

Thus the superdelocalizability, which was theoretically derived in the hyperconjugation consideration,^{3,4} is now acquired also in this configuration interaction treatment. Apart from the difference of the models of substitution mechanism, especially of the meanings of h involved in this interrelation, the superdelocalizability and the Z value were both proved to be given as the largest positive root of Eq. 2 corresponding to the positive and the negative values of Y_f , respectively.

If λ_f is equal to h , i.e., Y_f is equal to zero, Z_0 is written in a modified form as follows:

$$Z_0 = \sqrt{2} |C_f^f| \gamma + \sum_i^{occ-f} [(C_i^i)^2 / Y_i] \gamma^2. \quad (7)$$

Here the frontier electron density comes to determine a greater part of the reactivity.

For a nucleophilic reaction, though Brown did not treat this case, if one similarly defines the Z value according to condition A, one will easily find that the Z value is mathematically related to the superdelocalizability in the same way as for an electrophilic reaction.

§3. Mathematical Interrelations between Superdelocalizability and Z value-----

2. Homolytic Reaction

In order to clarify the interrelations between the indexes derived in various methods, an analogous treatment would be significant also for a radical reaction. Possible doublet configurations are classified into three classes: the configuration without charge transfer ($R\cdot \cdots ArH$, wave function Ψ_0), those corresponding to one-electron transfer from the i th occupied orbital of the attacked molecule to the half-occupied one of the attacking radical ($R^- \cdots ArH^+$, wave function Ψ_i), and those from the half-occupied orbital of the radical to the j th unoccupied one of the molecule ($R^+ \cdots ArH^-$, wave function Ψ_j). Inter-configurational integrals have the following values:

$$\left.
\begin{aligned}
\int \Psi_0 \mathbf{H} \Psi_k dv &= (C_r^*) \int \chi_R H \chi_r dv = C_r^* \gamma \beta, \\
&\quad (k: \text{every MO}), \\
\int \Psi_k \mathbf{H} \Psi_l dv &= 0, \\
&\quad (k, l: \text{every MO}; k \neq l),
\end{aligned}
\right\} \quad (8)$$

where \mathbf{H} is as usual the total Hamiltonian, expressed by the sum of effective one-electron Hamiltonians H , and χ_R is the half-occupied orbital of the attacking radical or the half-occupied quasi- π orbital at the transition state, which has the energy of $\alpha + \frac{1}{2}\beta$. Thus $F(Z)$ function is represented by

$$\begin{aligned}
F(Z) = Z - \sum_i^{\text{occ}} [(C_r^i)^2 \gamma^2 / (Z - Y_i)] \\
- \sum_j^{\text{unocc}} [(C_r^j)^2 \gamma^2 / (Z + Y_j)].
\end{aligned} \quad (9)$$

According to our theory the half-occupied quasi- π orbital lies between the highest occupied and the lowest unoccupied orbitals.⁴⁾ Then the stabilization energy in units of $(-\beta)$ at the transition state is

$$Z_0 = \left\{ \sum_i^{\text{occ}} [(C_r^i)^2 / (\lambda_i - h)] + \sum_j^{\text{unocc}} [(C_r^j)^2 / (h - \lambda_j)] \right\} \gamma^2. \quad (10)$$

If we put h equal to zero, this reduces to

$$Z_o = \left\{ \sum_i^{occ} [(C_r^i)^2 / \lambda_i] + \sum_j^{unocc} [(C_r^j)^2 / -\lambda_j] \right\} \gamma^2, \quad (11)$$

which is, namely, the superdelocalizability for a radical attack, also acquired in our hyperconjugation treatment of this problem.* In this connection Nagakura and Tanaka²⁾ state that the energy of the half-occupied level of most radicals is lower than that of the lowest unoccupied level of the attacked molecule and higher than that of the highest occupied level. Then in the configuration interaction treatment, it follows that the stabilization energy at the transition state, that is, the reactivity index, is expressed by Eq. 10 .

Thus, in a radical reaction, although not in heterolytic reactions, the configuration interaction treatment, no matter to which of the quasi- π orbital or the half-occupied orbital of the radical our attention may be paid,

* In more scarce cases, when the half-occupied level lies lower than the highest occupied one of the molecule, that is, $Y_f > 0$, Z_o is obtained as

$$Z_o = Y_f + (C_r^f)^2 \gamma^2 / Y_f$$

And when the half-occupied level stands higher than the lowest unoccupied one, a similar equation would be given. To these representations, only one or the other of the frontier orbitals is contributing, rather resembling the case of the Z value for heterolytic reaction.

may be said to present the identical index to the hyperconjugation treatment.

§4. Discussion on Charge Transfer Mechanism of Aromatic Substitution

In the preceding section we derived some mathematical correlations between the Z value and the superdelocalizability. As to heterolytic reactions the former corresponds to the most positive root of the equation $F(Z)$ for a negative value of Y_f , while the latter does so for its positive value.

In spite of the mathematical interrelations and the similar viewpoints of two theories, both of which attach great importance to the frontier orbital, Brown's theory⁵⁾ of aromatic substitution seems very different from the present authors' theory.^{1),3),4)} In this section we will make a comparative discussion of the two theories and point out some problems in the mechanism of aromatic substitution.

1. Extent of Charge Transfer

First, the discussion will be confined for simplicity to electrophilic substitution. According to Brown's theory the extent of the charge transfer, Δq_E , from the substrate to the electrophile at the transition state, is given,

regarding γ small, as

$$\Delta q_E = 1 - [2(C_{r'})^2 \gamma^2 / (h_E - \lambda_f)^2], \quad (12)$$

where h_E is the coefficient in the energy of the lowest unoccupied orbital of the electrophile at the transition state,

which is expressed as $\alpha + h_E \beta$. Inspection of the third

and the fifth columns of Table I and comparison of Eq.

(12) with the corresponding reactivity index,

Eq. 3, make it obvious that the larger the frontier

electron density, which is the intramolecular reactivity

index as seen in Eq. 3, on an atom is, the smaller the

quantity of charge transferred through the atom. That is

to say, a molecule suffers substitution reaction at the

position through which the least amount of charge is transferred

to the electrophile. This prediction would seem to

conflict with chemical intuition.

On the contrary, the extent of charge transfer in the present authors' theory is expressed for a small conjugation by

$$\Delta q_h = \sum_j^{occ} [2(C_{r'})^2 \gamma^2 / (\lambda_j - h_\pi)^2], \quad (13)$$

where h_π is the Coulomb integral of the quasi- π orbital,

being variable depending on Δq_h . With the progress of

reaction, that is, with the increase of γ , the charge

transfers continuously to the quasi- π orbital oozing out of the substrate according to Eq. 13 . This situation was explained in detail with the $(\Delta q_h - h, \gamma)$ diagram. At the transition state, where $h\pi$ was taken to be zero, as clearly seen in the third and the fourth columns of Table I, the extent of charge transfer is completely parallel in a molecule to the frontier electron density, that is, the most reactive position is also the one through which the largest amount of charge transfers.

For a nucleophilic reaction the circumstances are quite the same.

Thus we have encountered two mutually contradictory conclusions as to the relation of transferred charge and reactivity of one position. Further experiments will unravel this entanglement.

2. Energy Levels of Reagents

Condition A was set up by Nagakura and Tanaka in regard to the energy level of reagents in their isolated state, which has almost no concern with the transition state.²⁾ Brown, however, applied this rule also to the transition state. Indeed he formally distinguished the transition state by marking † from the separated state; however, by adopting condition A, γ^\ddagger for the transition

state was made a positive value. It might be dangerous to discuss the relative height of the unoccupied level of the electrophile at the transition state to the height of the highest occupied one of the substrate on the basis of the values in the separate state.

According to our theory, as it was stated in the earlier part of this chapter, in order for an electrophilic substitution to take place, the highest occupied level of the substrate must be higher than the quasi- π orbital energy which corresponds to the unoccupied level of the reagent. And, since the Coulomb integral of the quasi- π orbital is decided by its charge density in order to satisfy self-consistency, it is natural that it lies lower than the highest occupied level of the substrate at the stage where no charge is yet transferred.

3. Variation of Level Energy during Reaction

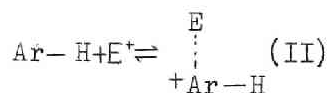
It is well expected that the energy of the reagent may vary considerably as the reaction proceeds. By introducing the self-consistent relation between the energy of the quasi- π orbital and its electron density that the former gets higher with the increase of the latter, the present authors indicated without difficulty that the energy of the quasi- π orbital rises during the progress of reaction in an electrophilic substitution and it falls in a nucleophilic substitution, and consequently that it approaches the Coulomb

energy of a carbon atom. Since mathematical expressions were given to these relations, one can easily trace the proceedings of the substitution reaction.

On the other hand, Brown did not take into account such a change in the energy level due to the transference of charge but rather that due to the solvation of the electrophile. But his discussion on the effects of solvation seems to be too complicated to formulate, and to make it difficult to follow after the completion of the reaction, including the feature of the activated complex, according to his theory.

4. Transition State

It does not seem clear in Brown's model what the activated complex, or the transition state, of the first step of his mechanism is. The first step is



Though in his formalism he distinguished the activated complex of this step from the charge-transfer complex (II), the state to which his conclusion actually pertains seems to correspond rather to the complex (II). To make a distinction between the two complexes may be difficult.

The definition of the transition state is clear in our

theory.³⁾ If one regards the three-center system consisting of the attacked carbon atom, the hydrogen atom, and the electrophile as the reaction center, the lowest occupied orbital of the system will be found to be a σ orbital in nature. The transition state was defined as the state at which this orbital has the maximum energy during the course of the reaction. Near the state the next orbital was proved to have a π character, and the stabilization energy due to the conjugation of this quasi- π orbital with the substrate was calculated as reactivity index. The super-delocalizability is a scale of this stabilization energy. This treatment would be rational in an aromatic substitution which implies dissociation and formation of a σ bond.

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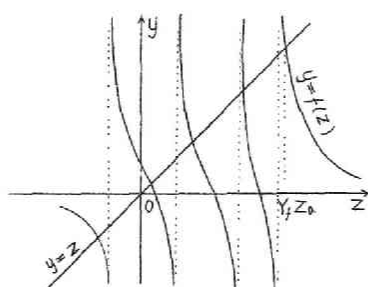


Fig. 1 Functional relations $y = Z$ and $y = f(Z)$ for $Y_f > 0$.

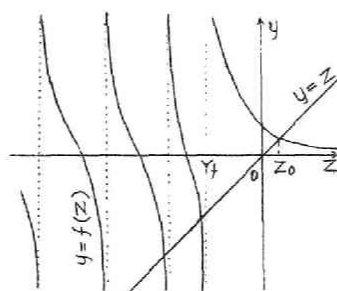


Fig. 2. Functional relations $y = Z$ and $y = f(Z)$ for $Y_f < 0$.

Table I. Frontier Electron Density and Extent of Charge Transfer Calculated by the Present Authors' Equation and by Brown's Equation.

Compound	Position	Frontier electron density	Δq_h by Eq. 13 in units of γ^2	Δq_E by Eq. 12 ^a
Benzene		0.333	0.750	0.760 ^b
Naphthalene	1	0.362	1.222	0.932
	2	0.138	0.889	0.974
Anthracene	9	0.387	2.500	0.945
	1	0.193	1.625	0.972
Naphthacene	2	0.097	1.125	0.986
	5	0.295	3.800	0.964
	1	0.112	2.000	0.986
Phenanthrene	2	0.067	1.400	0.992
	9	0.344	1.240	0.936
	1	0.231	1.160	0.957
	3	0.198	1.140	0.963
	4	0.110	0.960	0.979
	2	0.004	0.840	0.999

a Following values of parameters are assumed in accord with Brown: $h_E = 2.0$ and $\gamma = 0.6$.

b For the system which has doubly degenerate frontier levels Eq. 12 should be modified as follows:

$$\Delta q_E = 1 - 2 [(C_r^f)^2 + (C_r^{f'})^2] \gamma^2 / (h_E - \lambda_f)^2.$$

This value was calculated with this equation.

Chapter 6

Molecular Orbital Theory of Reactivities of Excited Molecules

§1. Introduction

In order to elucidate the mechanisms of reactions of conjugated or non-conjugated organic compounds which are in their ground state, a number of quantum mechanical, especially molecular orbital, studies have been performed and have achieved remarkable success in predicting theoretically their chemical reactivities¹⁻⁴⁾. In connection with the recent advance of techniques of photochemical investigation, chemical reactivities of electronically excited molecules have aroused our interest.

Because of the complicated characters and the multifariousness of reactions of excited molecules, only a few theoretical discussions have ever been made. As regards the problem of their self-dissociation, some qualitative discussions in terms of the potential energy curve have prevailed⁵⁾. For discussing the energy transfer reaction between an excited molecule and an unexcited one, the collision theory has prevailed as a powerful tool⁶⁾. On account of the lack in systematic experimental data and, in addition,

because of the difficulties in the theoretical treatment, only a few quantum chemical studies have been presented on excited molecules involved in the addition reactions of large organic molecules. Photopolymerization of hydrocarbons has been discussed in terms of free valence of the molecules in their lowest excited state. The intramolecular orientation in the reaction of anthracene or naphthacene has been explained well⁷⁾. But that of acenaphthylene has not been⁸⁾; free valence of its lowest excited states is greatest at positions 5 and 6, and, on the contrary, the photodimer of the compound is produced through positions 1 and 2.

In the present chapter, as was previously done with reference to the molecules in their ground state by the present authors^{9,10)} and by Brown¹¹⁾, the reactivities of excited molecules are assumed to be parallel with the π stabilization energy at the transition state due to the interaction of the molecule with the reagent (molecule, ion or radical) through the position of attack. Under this assumption the reactivity indexes are derived by the use of the molecular orbital method.

Reactions of an excited molecule with an unexcited molecule are classified into several cases from the point

of view of the spin multiplicity of reactants. The assumptions, the formulations and general considerations of the present molecular orbital treatments leading to the theoretical measures of reactivity will be described rather circumstantially in the first few cases, and in other cases only the indexes of reactivity derived will be given.

§2. Reaction of an Excited Triplet Molecule with an Unexcited Radical

First of all, attention is paid to the reaction of an excited triplet molecule (3A) with an unexcited radical (2B), where the numbers on the left shoulder refer to the multiplicity of the molecules. Here it would be rational for practical purposes in treating photochemical reactions to assume that the molecule 3A has only one excited electron. Then the wave functions of these molecules are written as follows:

$$\begin{aligned} \Psi(^3A) = & A \left[\dots (\psi_1 \alpha)^{n-3} (\psi_1 \beta)^{n-2} (\psi_{01})^{n-1} (\psi_{02})^n \right. \\ & \times \left. \begin{Bmatrix} \alpha(m-1) \alpha(m) \\ \beta(m-1) \beta(m) \\ (1/\sqrt{2}) \{ \alpha(m-1) \beta(m) + \beta(m-1) \alpha(m) \} \end{Bmatrix} \right] \\ \Psi(^2B) = & A \left[\dots (\phi_1 \alpha)^{n-2} (\phi_1 \beta)^{n-1} \begin{Bmatrix} (\phi_0 \alpha)^n \\ (\phi_0 \beta)^n \end{Bmatrix} \right] \end{aligned} \quad (1)$$

where ϕ_i and ϕ_j are the molecular orbitals of molecules A and B , respectively, whose numbering is schematically shown in Fig. 1, 01 and 02 denoting the lower and the higher half-occupied levels, of A , respectively, and (0) denoting the half-occupied level of the radical B ; m , an even integer, is the number of electrons of the molecule A and n , an odd number, is that of the radical B ; \hat{A} is the antisymmetrizing operator including the normalization constant; and each line in braces may constitute one wave function.

The states of the total system consisting of the triplet A and the doublet B would be a quartet and a doublet. But the quartet, which would be proved later to be less significant in this discussion, is abandoned. The doublet wave function for $M_s = 1/2^*$ is

$$\begin{aligned}
 {}^2\Psi_{1/2}[{}^2(AB)] &\equiv \Psi[0] = \hat{A} [\dots (\phi_i, \alpha)^{m-3} (\phi_i, \beta)^{m-2} \\
 &\dots (\phi_j, \alpha)^{m+n-4} (\phi_j, \beta)^{m+n-1} (\phi_{01})^{n-1} (\phi_{02})^n \\
 &\times (\phi_0)^{n+n} \{ (\alpha\beta + \beta\alpha) \alpha - 2(\alpha\alpha)\beta \} / \sqrt{6}].
 \end{aligned}
 \tag{2}$$

* M_s denotes the eigenvalue of S_z , the z component of the spin momentum operator.

where, for example, $\alpha\beta\alpha$ means $\alpha(m-1)\beta(m)\alpha(m+1)$. That for $M_s = -1/2$ is not written because the energetical argument is similar. Thus the state $\Psi[0]$ is assumed to correspond to the initial system of the reaction in question. If A and B are far separated from each other, the energy of the state is the same as that of the product function $\Psi(^1A) \cdot \Psi(^1B)$. The molecular orbitals may include all π ones and σ ones, but in this chapter we consider the reactions in company with only the π electron excitation, and hence σ orbitals will rationally be omitted as making an invariant framework.

At the transition state of the reaction the two molecules, 1A and 1B , will stay at a distance, making a weak interaction through the atoms at which the reaction takes place. This interaction is assumed to be a kind of $\pi-\pi$ conjugation and in this simple LCAO MO approach it will be represented by a small resonance integral $\gamma\beta$ between the atomic π orbitals γ and s of the reactants, A and B , respectively, where β is the resonance integral of the $C-C\pi$ bond in benzene. This perturbation makes the initial state $\Psi[0]$ come to the direct or indirect interaction with various electronic configurations of the combined system. Of these configurations only those, which have energy matrix

elements with the initial state in scope of the simple LCAO MO approximation, are taken into account. This means that the configurations (of course, doublet and $M_s = 1/2$) in which one electron transfers from 3A to 3B and vice versa have concern with the transition state of the reaction, whereas those which correspond to intramolecular one-electron transitions do not.

Under these assumptions the electron configurations to be taken into account are those corresponding to the following one-electron transfers, represented by $l \rightarrow m$, from an occupied or half-occupied orbital, l , to an unoccupied or half-occupied orbital, m :

$$\begin{aligned}
 &02 \rightarrow (0), 02 \rightarrow (j'), 01 \rightarrow (0), 01 \rightarrow (j') \\
 &i \rightarrow (0), i \rightarrow (j'), (0) \rightarrow 01, (0) \rightarrow 02 \\
 &(0) \rightarrow i', (j) \rightarrow 01, (j) \rightarrow 02, (j) \rightarrow i'
 \end{aligned} \tag{3}$$

where

$$\begin{aligned}
 i &= 1, 2, \dots && (\text{occupied orbitals of } {}^3A) \\
 i' &= 1', 2', \dots && (\text{unoccupied orbitals of } {}^3A) \\
 (j) &= (1), (2), \dots && (\text{occupied orbitals of } {}^3B) \\
 (j') &= (1'), (2'), \dots && (\text{unoccupied orbitals of } {}^3B)
 \end{aligned}$$

They are schematically illustrated in Fig. 2. For an illustration, the configuration associated with the transfer

$O2 \rightarrow (0)$, will have the following wave function:

$$\begin{aligned} \psi [O2 \rightarrow (0)] \\ = A \left[\dots (\phi_o \alpha)^{n+n-2} (\phi_o \beta)^{n+n-1} (\psi_o \alpha)^{m+n} \right] \end{aligned} \quad (4)$$

The energy matrix element between these configurations and the initial state can be expressed in terms of the integral $\gamma\beta$. For example,

$$\left| \int \psi^* [O2 \rightarrow (0)] H \psi (0) d\tau \right| = |c_r^{o2} d_s^o \gamma\beta| \quad (5)$$

where c_r^k and d_s^l are the coefficient of the atomic orbitals r and s in the molecular orbital k and l of the molecules A and B , respectively.

The transition state of the reaction is the lowest energy state resulting from the interaction mentioned above. The difference in π electronic energy, i.e. the stabilization energy, between the initial state and the transition state, was assumed in the preceding section to parallel the activation energy of the reaction, and accordingly the reactivity of the excited molecule. This stabilization energy would be expanded in powers of γ by regarding it to be small. There arise three main subcases according to the mutual relation of the energy levels $O1$ and $O2$ of the molecule 3A and (0) of the molecule $^2B^*$. In the following

* Some rare cases, for instance, $\gamma_{o,o2} > 0$ or $\gamma_{o,1,0} > 0$, are not included for the sake of brevity.

$\gamma_{k,l}$ denotes the energy in units of $(-\beta)$ turned out in one electron transfer from the molecular orbital k of the one molecule to the molecular orbital l of the other one. That is, $\gamma_{k,l}$ is positive if the level k is higher than the level l and vice versa. Thus we reach the final reactivity indexes of excited molecules.

(a) If $\gamma_{02,e} > \gamma_{01,e} > 0$, that is, if the half-occupied level of the molecule B lies between the levels 01 and 02 of A and is nearer to 01 than to 02 as is shown in Fig.3 (a), the stabilization energy to the second order of γ is written in the following expression**:

$$\Delta E \left[\gamma_{02,e} + \frac{(3/2)(C_{Y^{02}})(d_s^0)^2}{\gamma_{02,e}} \gamma^2 \right] (-\beta) \quad (6)$$

From this formula some general conclusions on reactivities of excited molecules may be derived. In most reactions between unexcited molecules, terms do not appear in the second order of γ , whereas in Eq. 6 the term in zero order exists. The appearance of the zero order term is

** In general the stabilization energies for each M_s component may differ from each other. In the surroundings of reaction no magnetic field being applied, no specialization of the component is possible and the mean of all components would be significant as a real stabilization energy. In this case the energy for $M_s=1/2$ is the same as that for $M_s=-1/2$; also the mean energy becomes the same.

universal in all the following cases and subcases, making clear the reason why the reactions including excited molecules proceed so fast. The difference in reactivity of several excited molecules would thus dominantly be decided by this term. The intramolecular orientation, on the other hand, depends on the term in the second order. More minutely, so far as attention is paid to the lowest excitation of the molecule A as is expected in real photochemical reactions of conjugated molecules, the atom where $(C_r^{o2})^2$, the frontier electron density for a nucleophilic attack in the ground state, is the greatest is the most reactive in an excited molecule. The coefficient $(3/2)$ is characteristic to the triplet A molecule. If the molecule A is excited in the singlet state it amounts to $(1/2)$, as will be mentioned in the section 4. . The difference would not necessarily mean the difference in reactivity of these two states, since the approximation is too simple to discuss at this point, on which there will be some discussion in a later section.

To the transition state the electron configuration corresponding to the one-electron transfer $O2 \rightarrow (O)$ has the greatest contribution, since the other configurations have the first contribution to ΔE in the fourth order. Therefore, the direction of charge transfer is from molecule A

to molecule B.

(b) If $\gamma_{o,o1} > \gamma_{o2,o} > 0$, i.e., if the half-occupied level of 2B lies between the levels 02 and 01, and nearer to 02 than to 01, as shown in Fig. 3 (b), then

$$\Delta E = \left[\gamma_{o,o1} + \frac{(3/2)(C_{r^{o1}})^2 (d_s^o)^2}{\gamma_{o,o1}} r^2 \right] (-\beta) \quad (7)$$

In this subcase also the rate of reaction is great and the intramolecular orientation of the excited molecule is controlled by $(C_{r^{o1}})^2$, the frontier electron density for an electrophilic attack in the ground state. The most contributive configuration in this subcase corresponds to the transition $(0) \rightarrow 01$, resulting in a charge transfer from B to A.

(c) If $\gamma_o = \gamma_{o2,o} = \gamma_{o,o1} > 0$, i.e., if the level (0) is just in the midst of the levels 01 and 02, as shown in Fig. 3 (c), then

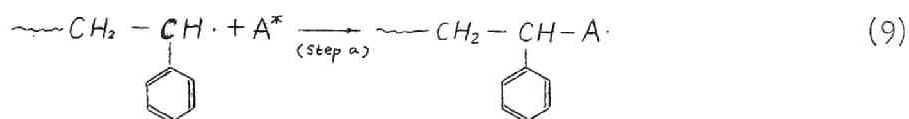
$$\Delta E = \left[\gamma_o + \frac{(3/2) [(C_{r^{o1}})^2 + (C_{r^{o2}})^2] (d_s^o)^2}{\gamma_o} r^2 \right] (-\beta) \quad (8)$$

A large rate constant is confirmed also in this subcase, and $[(C_{r^{o1}})^2 + (C_{r^{o2}})^2]$, the frontier electron density for a radical attack in the ground state, comes to the point.

So far as alternant hydrocarbons are concerned, however,

the equality $(C_{r''})^2 = (C_{r'''})^2$ holds in the simple LCAO MO approximation, so that in all subcases and the following cases the most reactive position in a molecule in its lowest excited state is the same as that in the ground state. This explains the great reactivity of meso position of anthracene. Further experimental studies are anticipated with respect to the intramolecular orientation in nonalternant hydrocarbons and heterocyclic compounds where the equality mentioned above no more exists.

Here a comparison with experimental data may be given. Excited triplet anthracene was reported by Norrish et al.¹²⁾ to enter into the chain of polymerization of styrene in the following way:



Observed rate constant, k_a , and calculated π stabilization energy ΔE are tabulated in Table I. The stabilization in the reaction a is calculated by using Eq. 8. Those of other reactions in which only molecules in their ground state participate are given by the usual formula for stabilization energy¹⁰⁾:

$$\Delta E = \left[\sum_j^{unocc} \sum_i^{all} v_i - \sum_j^{oco} \sum_i^{all} (2 - v_i) \right] \\ \times \frac{(C_{r^i})^2 (d_{s^j})^2}{Y_{ji}} \gamma^2 (-\beta) \quad (10)$$

where v_i is the number of electrons in the i th molecular orbital of A. The extraordinary great magnitude of rate constant of reaction a is well understood in connection with the presence of the zero order term. Further, the position 9 is the most active, at which anthracene would enter into the polymer chain. An appropriate choice of the value of γ ($=0.7$) makes the $\log k_s - \Delta E$ plots practically linear.

The wave functions (Eq. 1) of 3A and 2B may be combined so as to construct a quartet instead of the doublet (Eq. 2). The quartet state has matrix elements with some configurations in Eq. 3, only to give the stabilization energy in the second order. Because of the lack of the zero order terms and, accordingly, because of the instability of the transition state, reactions would not be considered to proceed by way of the quartet transition state.

§3. Reaction of an Excited Triplet Molecule with an Unexcited Molecule

The reaction of an excited triplet molecule (3A) with

an unexcited singlet molecule (1B)* now comes to our attention. Discussions are almost alike, so that the only important formulas would be summarized in this case and in the following cases. The numbering of molecular orbitals is illustrated in Fig. 4. The states of the combined system at the initial stage of reaction are represented by a set of three triplet wave functions, one with $M_s = 1$, one with $M_s = 0$ and the other with $M_s = -1$, as follows:

$$\left. \begin{aligned}
 {}^3\Psi_1 &= A [\dots (\psi_{o1})^{m+n-1} (\psi_{o2})^{m+n} \\
 &\quad \times \alpha (m+n-1) \alpha (m+n)] \\
 {}^3\Psi_0 &= A [\dots (\psi_{o1})^{m+n-1} (\psi_{o2})^{m+n} \\
 &\quad \times \{ \alpha (m+n-1) \beta (m+n) \\
 &\quad + \beta (m+n-1) \alpha (m+n) \} / \sqrt{2}] \\
 {}^3\Psi_{-1} &= A [\dots (\psi_{o1})^{m+n-1} (\psi_{o2})^{m+n} \\
 &\quad \times \beta (m+n-1) \beta (m+n)]
 \end{aligned} \right\} \quad (11)$$

Electronic configurations which are taken into account in the perturbation calculation are summarized in Fig. 5 with illustrations. Each M_s component of the functions 11 will have matrix elements with the same M_s component of the wave

* The singlet molecule 1B may be an ion whose spin is singlet.

functions for the configurations in Fig. 5. Then the stabilization energy* is obtained as follows, according to the mutual relation of energy levels:

(a) If $\gamma_{o2,1v}$ is positive and the most positive of all γ'_s , then

$$\Delta E = \left[\gamma_{o2,1v} + \frac{(C_r^{o2})^2 (d_s^{1v})^2 \gamma^2}{\gamma_{o2,1v}} \right] (-\beta) \quad (12)$$

This is the case for most electrophilic reagents (cations) serving as 'B'.

(b) If $\gamma_{ko,oi}$ is positive and the most positive of all γ'_s , then

$$\Delta E = \left[\gamma_{ko,oi} + \frac{(C_r^{oi})^2 (d_s^{ko})^2 \gamma^2}{\gamma_{ko,oi}} \right] (-\beta) \quad (13)$$

Most nucleophilic reagents (anions) as 'B' are included in this subcase.

(c) If $\gamma_{o2,1v} = \gamma_{ko,oi}$, and they are positive (then of course the most positive), then, putting them equal to γ_0 ,

$$\Delta E = \left[\gamma_0 + \frac{\{ (C_r^{o2})^2 (d_s^{1v})^2 + (C_r^{oi})^2 (d_s^{ko})^2 \} \gamma^2}{\gamma_0} \right] (-\beta) \quad (14)$$

Such a conjugated molecule as has its lowest excitation energy smaller than the excitation energy to the triplet of

* Each M_s component gives the same stabilization energy, and the mean is, therefore, the same.

the molecule A would be classified in this subcase.

(d) If all γ'_s are negative, then

$$\Delta E = \left[\sum_j^{\text{unocc}} \sum_i^{\text{all}} \nu_i - \sum_j^{\text{occ}} \sum_i^{\text{all}} (2 - \nu_i) \right] \frac{(C_r^i)^2 (d_s^j)^2 \gamma^2}{\gamma_{ji}} (-\beta) \quad (15)$$

In this subcase the stabilization energy begins in the second order terms, predicting a slow rate in the process of reaction.

(e) If $\gamma_{02,1v} = 0$ and the others are negative, then

$$\Delta E = \left[|(C_r^{02})(d_s^{1v})| \gamma + \left\{ \sum_j^{\text{unocc}} \sum_i^{\text{all}} \nu_i - \sum_j^{\text{occ}} \sum_i^{\text{all}} (2 - \nu_i) \right\}' \frac{(C_r^i)^2 (d_s^j)^2 \gamma^2}{2 \gamma_{ji}} \right] (-\beta) \quad (16)$$

where the mark ' on the summation tells to omit the set ($j = 1v$, $i = 02$).

(f) If $\gamma_{h0,01} = 0$ and others are negative, then,

similarly

$$\Delta E = \left[|(C_r^{01})(d_s^{h0})| \gamma + \left\{ \sum_j^{\text{unocc}} \sum_i^{\text{all}} \nu_i - \sum_j^{\text{occ}} \sum_i^{\text{all}} (2 - \nu_i) \right\}' \frac{(C_r^i)^2 (d_s^j)^2 \gamma^2}{2 \gamma_{ji}} \right] \quad (17)$$

' indicating the neglect of the set ($j = h0$, $i = 01$).

(g) If $\gamma_{02,1v} = \gamma_{h0,01} = 0$ and others are negative, we obtain

$$\Delta E = \left[\sqrt{(C_r^{02})^2 (d_s^{1v})^2 + (C_r^{01})^2 (d_s^{h0})^2} \gamma + \left\{ \sum_j^{\text{unocc}} \sum_i^{\text{all}} \nu_i - \sum_j^{\text{occ}} \sum_i^{\text{all}} (2 - \nu_i) \right\}' \times \frac{(C_r^i)^2 (d_s^j)^2 \gamma^2}{2 \gamma_{ji}} \right] (-\beta) \quad (18)$$

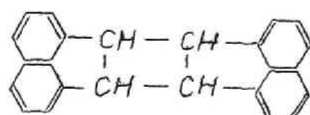
neglecting in the summation the sets ($j = h_0$, $i = 01$) and ($j = 1v$, $i = 02$) In the latter three subcases the stabilization is of the first order, and for the lowest excited molecule the frontier electron density controls a main part of the reactivity indexes. The subcase g includes reactions of an excited molecule with an unexcited molecule of the same kind.

The photodimerization of aromatic hydrocarbons has been considered to pass through the following mechanism:



Though the detail of the intermediate (AA^*) is not clear, assuming the present type of complex for the transition state of step b, one can discuss the reactivity of this reaction as belonging to the subcase g. In Table II calculated values of the π stabilization energy are collected. In that table, reagents are assumed to make two weak bondings through two meso positions, as illustrated in Fig. 6; the assumption of one bonding would only need to divide the values by the factor 2. Anthracene is well known to make a photodimer at 9 and 10 positions, in accord with our calculation. Also in other polyacenes the most central meso-position have the largest stabilization energy. This result

is compatible with the experiment¹³⁾. Bowen and Marsh¹⁴⁾ studied the photodimerization of acenaphthylene, finding that the structure of the photodimer was



This finding was first theoretically discussed by Crawford and Coulson⁸⁾. They calculated the free valence of this molecule in its lowest excited state and found that the values of positions 5 and 6 (0.62) are greater than those of positions 1 and 2 (0.57), which conflicted with the above experimental results. Thus they stated that the free valence is not a sufficient guide to reactivity. Recently this experiment has been interpreted successfully by Fukui et al. in terms of the frontier electron density for a radical reaction¹⁵⁾. The frontier electron density of positions 1 and 2 is greater than that of positions 5 and 6. In that paper the excited acenaphthylene was regarded as an ordinary radical reagent attacking an acenaphthylene molecule in the ground state. At this time it would be interesting to apply the present theory which involves an explicit consideration of the excitation. This belongs to the subcase g. As is seen in Table II the stabilization

energy of the reaction through pairs of positions 1-1 and 2-2 is greater than that through 5-5 and 6-6, in accordance with the experiment.

In intermolecular comparison it is said that the ease of photodimerization is greater in pentacene than in anthracene¹³). But this is not a direct comparison of the rate constant k_b of the step b but a rough estimation from the amount of dimers produced. The total rate of dimer formation would be affected not only by the rate constant k_b but also by various competitive reactions such as the collisional or spontaneous degradation of the excited A molecule, dissociation of (AA*), and so forth. To measure and compare the rate constant with calculated stabilization energy would be interesting.

§4. Some Other Kinds of Reaction

Reaction of an Excited Singlet Molecule with an Unexcited Radical.--The reaction of an excited singlet molecule (1A) with an unexcited radical (2B) can be discussed in a way similar to that of a triplet molecule (3A) mentioned in the preceding reaction. The doublet wave function for $M_S = 1/2$ of the combined system is, in place of Eq. 2 in the triplet case,

$$\psi [0] = A \left[\dots (\phi_{o1})^{m-1} (\phi_{o2})^n (\phi_o)^{m+n} \right. \\ \left. \times \{ (\alpha\beta - \beta\alpha) \alpha \} / \sqrt{2} \right] \quad (20)$$

Also, we are led to the same equations as Eqs. 3, 4 and 5, excepting that the numerical coefficient in the second term should be read (1/2) in this case, instead of (3/2). The meanings of the frontier electron density and the direction of charge transfer in each subcase are entirely the same as in section 2 and therefore discussions may be omitted for brevity.

Reaction of an Excited Singlet Molecule with an Unexcited Molecule.--The method and the results of the treatment for this kind of reaction is exactly the same as that in section 3 if only the wave function, Eq. 11, is replaced by the following equation:

$$\psi_o = A \left[\dots (\phi_{o1})^{m+n-1} (\phi_{o2})^{m+n} \{ \alpha(m+n-1) \right. \\ \left. \times \beta(m+n) - \beta(m+n-1) \alpha(m+n) \} / \sqrt{2} \right] \quad (21)$$

Eqs. 12 to 19 are also valid in this case.

Reaction of an Excited Molecule with Another Excited Molecule.--We derived also the equations giving the stabilization energy in a reaction of an excited molecule (singlet

or triplet) with another excited molecule (singlet or triplet) in a similar way. But as they are less meaningful for practical purposes and rather intricate, we do not give their explicit forms. It would be noteworthy that in this case also the frontier electron densities decide the intramolecular orientation.

§5. Discussion

We have derived formulas giving the π stabilization energy and the reactivity index, discussing the rate of reactions of excited molecules. But we do not, at all, regard this theory as complete but merely as a simple pioneering attempt in the molecular orbital method; the assumptions included may have to be subjected to some improvements in future. For discussing the difference in rate constant caused by the difference in multiplicity of states, interactions of electrons should be explicitly taken into account. For discussing various dissociation reactions, attention would have to be paid to σ electrons in the bond to be broken. Furthermore, in order to understand all the figures of reactions of an excited molecule, discussions on relations between various elementary steps involved in the reaction would be expected.

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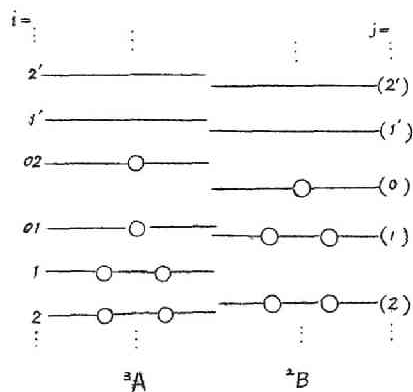


Fig. 1. Numbering of molecular orbitals.

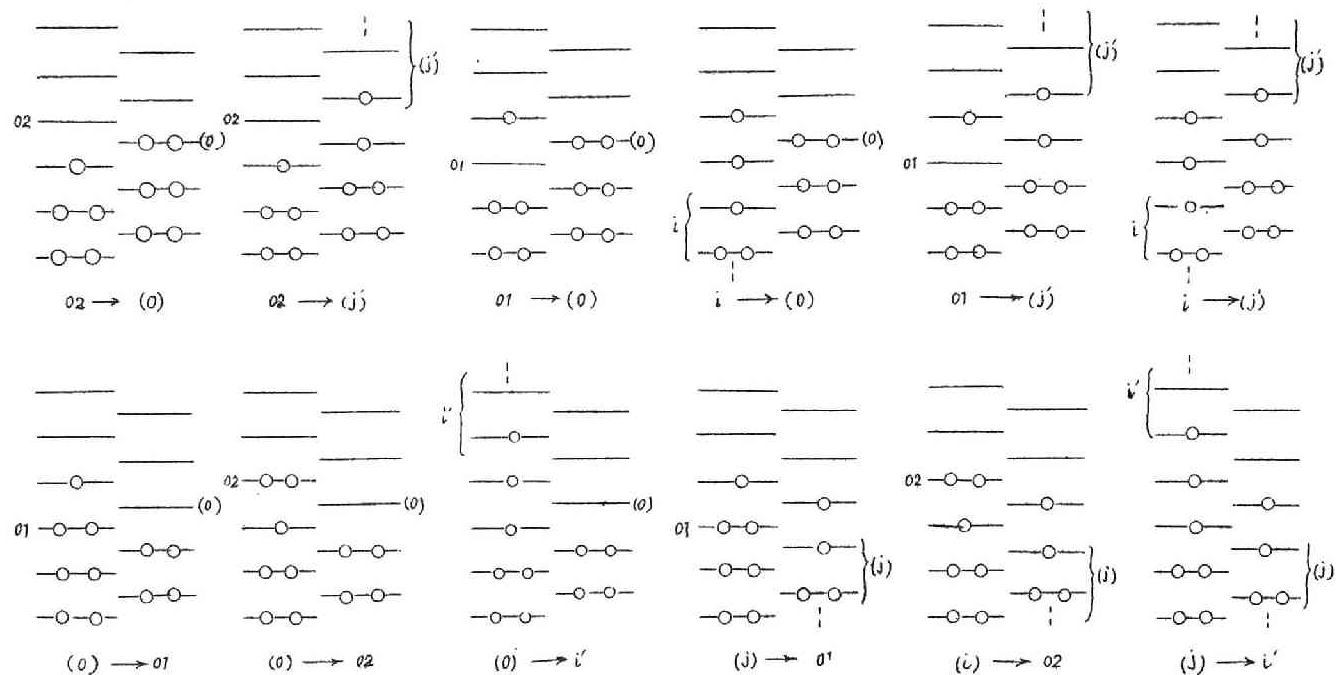


Fig. 2. Electronic configurations taken into account.

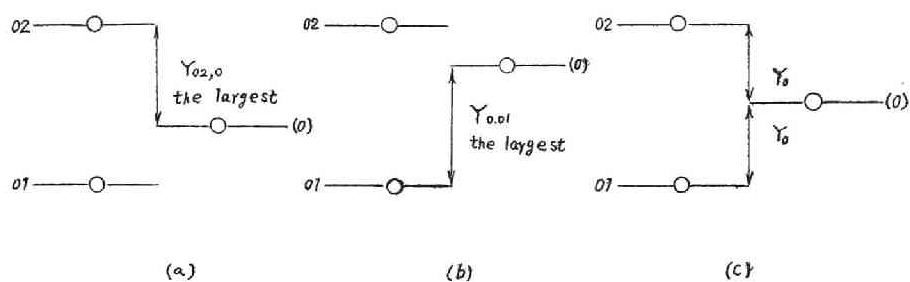


Fig. 3. Mutual relation of molecular levels.

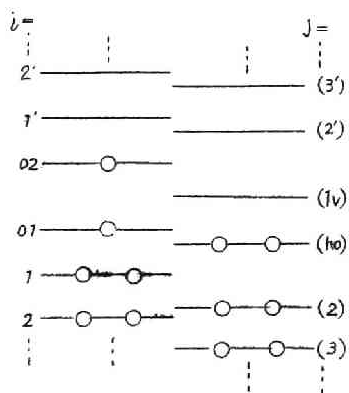


Fig. 4. Numbering of molecular orbitals.

1v and ho mean the lowest unoccupied and the highest occupied orbitals, respectively.

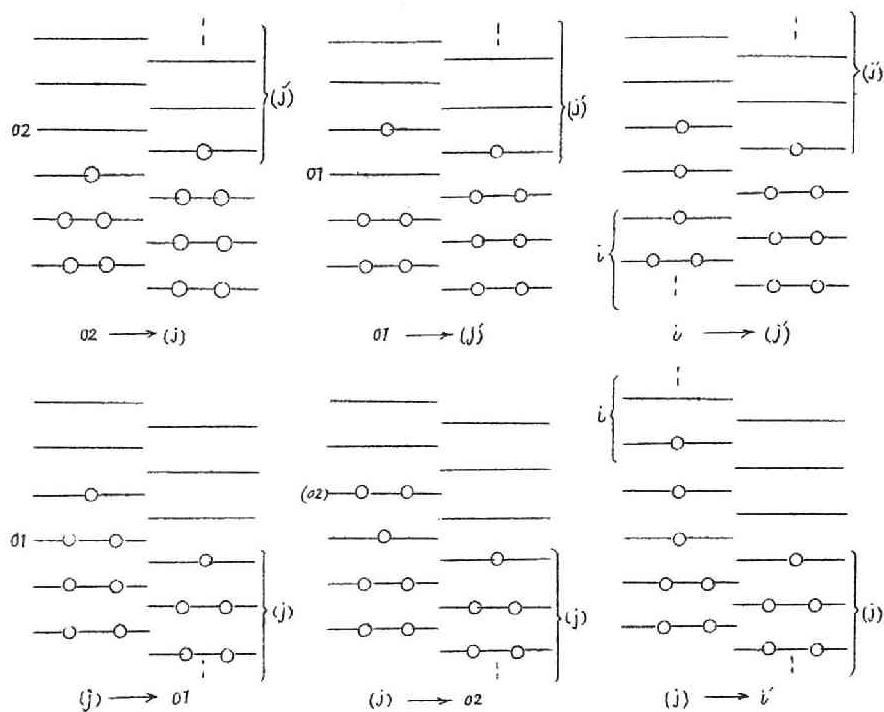


Fig. 5. Electronic configurations taken into account.

$i = 1, 2, \dots$ (occupied orbitals of 3A);
 $i' = 1', 2', \dots$ (unoccupied orbitals of 3A);
 $j = 1, 2, \dots$ (occupied orbitals of 3B); and
 $j' = 1', 2', \dots$ (unoccupied orbitals of 3B).

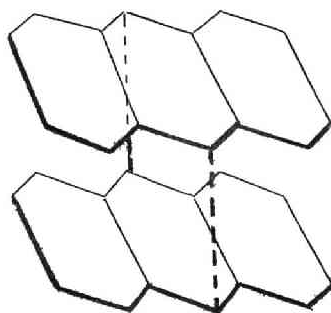


Fig. 6. Model of transition state of photodimerization of anthracene.

Table I. Rate Constant and π Stabilization Energy of Polymerization of Styrene
Reaction^{a)}

	Rate constant ^{b)} $k(1. \text{ mol}^{-1} \text{ sec}^{-1})$	π Stabilization energy (in units of $-\beta$) ^{c)}
$R\cdot + {}^3A \rightarrow RA\cdot$	$\sim 10^4$	$0.414 + 0.801\gamma^2$ (position 9) $0.414 + 0.400\gamma^2$ (position 1) $0.414 + 0.200\gamma^2$ (position 2)
$R\cdot + A \rightarrow RA\cdot$	3.4×10^2	$0.926\gamma^2$
$R\cdot + M \rightarrow R\cdot$	1.2×10^2	$0.932\gamma^2$
$RA\cdot + M \rightarrow R\cdot$	0.8	$0.739\gamma^2$

a) Abbreviation, $R\cdot$: polymer radical of styrene; 3A : triplet anthracene;
A: anthracene; M: styrene.

b) Taken from Ref. 10.

Table II. π Stabilization Energy in Photodimerization of Polyacenes and Acenaphthylene

Compound	Pairs of positions to react with	π Stabilization energy (in units of $-\beta$)
Anthracene	9-9, 10-10 (central)	0.547 γ
	1-1, 4-4 (end)	0.273 γ
Naphthacene	5-5, 12-12 (central)	0.417 γ
	1-1, 4-4 (end)	0.159 γ
Pentacene	6-6, 13-13 (central)	0.400 γ
	5-5, 14-14 (end)	0.299 γ
Acenaphthylene	1-1, 4-4 (end)	0.100 γ
	1-1, 2-2	0.568 γ
	5-5, 6-6	0.375 γ

Chapter 7

On Cross Termination in Radical Polymerization

§1. Introduction

It is well known that at the termination process in the copolymerization of vinyl compounds the ϕ value in most cases is larger than unity, that is to say, radicals of different kinds are easier to react with each other than those of the same kind.

In the copolymerization of two vinyl monomers, say, A and B, the termination process consists of the following three kinds of reaction:



and the ϕ value is defined as follows:

$$\phi = k_{AB} / \sqrt{k_{AA} k_{BB}} \quad (4)$$

As is seen in the second column of Table I, in the first three systems of Table II k_{AB} is larger than k_{AA} and k_{BB} and in the styrene-*p*-methoxystyrene system the order is $k_{AA} > k_{AB} > k_{BB}$.

Molecular orbital theories of chemical reaction, which have successfully elucidated the problems of vinyl polymerization, 1-3) have not yet been applied to this point. The localization method, for instance, can explain neither the order of rate constant nor the ϕ value, the total localization energies of the three kinds of reaction being given as follows:

$$\begin{aligned} L(\text{reaction 1}) &= L_A + L_A \\ L(\text{reaction 2}) &= L_B + L_B \\ L(\text{reaction 3}) &= L_A + L_B \end{aligned} \quad (5)$$

The order indicated in this method is as an inevitable consequence $k_{AA} > k_{AB} > k_{BB}$ or $k_{AA} < k_{AB} < k_{BB}$; furthermore, the difference ΔL as given by:

$$\begin{aligned} \Delta L &= L(\text{reaction 3}) - [L(\text{reaction 1}) \\ &\quad + L(\text{reaction 2})]/2 \end{aligned} \quad (6)$$

is always zero, this meaning that ϕ is unity, which conflicts with the experience. In Eqs. 5, L_A and L_B mean the localization energies of α -carbon of polymer radicals. The situation is the same for free valence.

§2. Calculation of π Conjugation Energy and Results and Discussion.

The present authors have tried an approach to this problem in terms of π -conjugation energy and qualitatively interpreted the ease of cross termination. That is to say, assuming as was done in their previous paper¹⁾ that at the transition state of recombination reaction* a weak π conjugation takes place between vinyl α -carbons of the polymer radical end[†] as is shown in Fig. 1, and that the stabilization energy due to this conjugation determines the rate constant, we calculated the π -conjugation energy E both by the perturbation method and by solving the secular determinant. Values of E are collected in Table I, and in Table II are listed experimental ϕ values and the corresponding differences ΔE of the conjugation energy:

$$\Delta E = E_{AB} - \{ (E_{AA} + E_{BB}) \} / 2 \quad (7)$$

In Tables I and II γ denotes for the exchange integral between α -carbons in units of β , where β is the standard resonance integral.

* In the present treatment the contribution of disproportionation is neglected. Discrepancies of conjugation energy with the rate constant in Table I may partly be attributed to this.

† The hybridization of the carbon atoms of the radical ends would vary from sp^2 to sp^3 as the reaction proceeds. In the transition state it would be reasonable to assume an sp^2 hybridization since the two end carbons are separated farther than in the products.

On inspection of the third column of Table I, one can rationally explain the order of rate constants $k_{AB} > k_{AA}$, k_{BB} in the first three systems: for example, the $k_{\text{styrene-methyl acrylate}}$ value corresponds to a large term of zero order, whereas the small $k_{\text{styrene-styrene}}$ and $k_{\text{methyl acrylate-methyl acrylate}}$ values correspond to smaller terms of first order. In the styrene-*p*-methoxystyrene system, on the contrary, the extreme small value (0.068) of the first order term of E_{AB} would be surpassed by the terms of the first order of E_{AA} and E_{BB} . In the secular determinant method a smaller conjugation ($\gamma = 0.3$) also gives a practically good result, while the larger conjugation ($\gamma = 1$) does not, as is seen in Table I. This seems to indicate that the ease is determined at an earlier stage of π conjugation.

In Table II differences of π -conjugation energy [cf. Eq. 7] elucidate satisfactorily the ϕ values of the four systems, their relationship being nearly linear; here also, the smaller conjugation is preferred.

Parameters used in the calculation are for the nitrile group, $\alpha_N = \alpha + \beta$, $\beta_{CN} = \beta$; for the carbonyl group, $\alpha_O = \alpha + 2\beta$, $\beta_{CO} = \sqrt{2}\beta$, $\alpha_C = \alpha + 0.2\beta$; for the methoxy group $\alpha_{OCH_3} = \alpha + 0.5\beta$, $\beta_{OCH_3} = 0.55\beta$, $\alpha_C = \alpha + 0.05\beta$;

and $\alpha_{C'} = \alpha - 0.2\beta$, where C' is the carbon attached to the methyl group.

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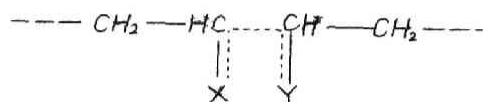


Fig. 1. Model of transition state of coupling.

Table I

Rate Constant and Conjugation Energy of Termination of
Vinyl Polymerization

Radical pairs ^a A-B	Rate constant k_{AB} , l./mole sec. ^b	Conjugation energy E ^c		
		Perturbation	Secular determinant	
			$\gamma = 0.3$	$\gamma = 1$
MMA-St	2.9×10^8	0.239	0.427	1.392
MMA-MSt	1.2×10^8	0.306	0.459	1.376
St-MA	$\begin{cases} 9.0 \times 10^7 \\ 6.1 \times 10^7 \end{cases}$	0.329	0.488	1.422
MMA-MMA	2.4×10^7	0.802γ	0.322	1.309
St-St	1.7×10^7	1.000γ	0.376	1.436
MA-MA	$\begin{cases} 9.4 \times 10^6 \\ 4.3 \times 10^6 \end{cases}$	0.930γ	0.316	1.319
St-MSt	4.3×10^6	0.068	0.368	1.409
MSt-MSt	1.06×10^6	1.088γ	0.346	1.379

^a Abbreviations: MMA = methyl methacrylate, St = styrene, MSt = *p*-methoxystyrene, MA = methyl acrylate.

^b These values are quoted from Burnett.⁴⁾

^c In units of (- β).

Table II

 ϕ Value and Conjugation Energy Difference

System	ϕ^a	Conjugation energy difference ΔE^b		
		Perturbation	Secular determinant	
			$\gamma = 0.3$	$\gamma = 1$
MA + St	50	0.329	0.284	0.089
MMA + MSt	24	0.306	0.250	0.064
MMA + St	14	0.239	0.156	0.039
St + MSt	1	0.068	0.014	0.003

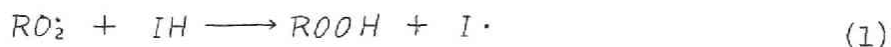
^a Data of Burnett.⁴⁾^b In units of $(-\mathcal{P})$.

Chapter 8

Electronic Structures and Antioxidizing Activities

§1. Introduction

Autooxidation of several organic substances --- for instance, petroleum hydrocarbons, rubber and oil ---- has long been studied by many authors and has been well known as it proceeds through a radical chain reaction mechanism. Antioxidants such as phenols and substituted anilines work as chain-breaking inhibitors of peroxy radical:



and the radical $I \cdot$ from the inhibitor is less reactive and can hardly initiate a new chain reaction, as was first presented by Bolland et al.¹⁾.

From the theoretical point of view Fueno et al.²⁾ studied in the simple LCAO MO approximation of π electronic systems the relation between the highest occupied electronic levels and the oxidation potentials of various hydroxy derivatives of aromatic hydrocarbons and also the relation between the highest occupied levels or the stabilization energies of the transition complexes and the antioxidanting efficiencies.

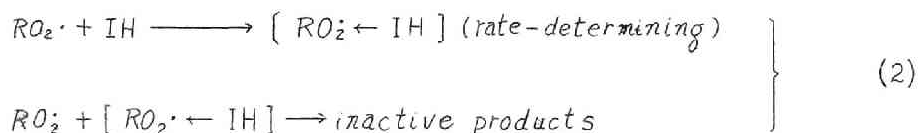
In the present chapter antioxidanting activities of

phenols will be discussed in the connection of their σ electronic structures as well as of their π electronic structures.

§2. π Electronic Structures and Antioxidizing

Activities of Substituted Phenols

According to Boozer and Hammond et al.³⁻⁵⁾ the overall inhibition reaction, Eq.1, does not necessarily mean that the rate-determining step of inhibition is the hydrogen abstraction reaction, for N-methylaniline-N-d and diphenylamine-N-d showed the same efficiency as the undeuterated compounds. They proposed the following mechanism:



$[RO_2 \leftarrow IH]$ is a molecular complex between the inhibitor and the radical and the first complex-formation step is rate-determining. On the nature or structure of the complex no decisive fact seems to have been revealed.

In this section π molecular orbital calculation will be given and some discussions on the complex will be delivered. Parameters of the Coulomb and the resonance integrals used in this section are as follow: $\alpha_o = \alpha + 0.51\beta$, $\beta_{o-c'} = 0.57\beta$, $\alpha_{c'} = \alpha + 0.05\beta$ ⁶⁾; $\alpha_{CH_3} = \alpha + 3\beta$,

$$\beta C^{\bullet}-CH_3 = 0.7\beta, \quad \alpha C^{\bullet} = \alpha - 0.1\beta \quad \text{and}$$

$$\alpha_C(\text{adj. to t-butyl}) = \alpha - 0.2\beta.$$

Tert-butyl group is taken as a purely inductive group, while methyl group is partly inductive and partly hyperconjugative one, hyperconjugation being treated by well-known one-atom model.⁷⁾

The Highest Occupied π Level. ----- It has been often recognized that no matter what is the structure of a molecular complex the ionization potential of the electron donor and the electron affinity of the acceptor decide the ease of complex formation⁸⁻¹⁰⁾. Some comparisons¹¹⁾ of the oxidation potentials and the antioxidizing efficiencies (induction periods) supported the possibility. In the molecular orbital sense the ionization potential is the absolute value of the energy of the highest occupied π orbital. We compared the calculated energies of the highest occupied π levels with the antioxidizing relative molecular potencies of 2,4,6-substituted phenols measured by Rossenwald et al.¹²⁾, as is shown in the third and the fourth columns of Table I. In the table methyl and/or tert-butyl substituted phenols are divided into three classes----one consisting of 2,6-di-tert-butyl phenols, another of 2-tert-butyl phenols and the other consisting of phenols with no tert-butyl group at 2 and 6

positions. The parallelism between the potency and the energy of the highest occupied π level is observed within each class of compounds, suggesting that the smaller ionization potential will result in an easier formation of the complex and therefore result in a larger potency. Fueno et al.²⁾ also compared the highest occupied levels and anti-oxidizing efficiencies of some hydroxy derivatives of aromatic hydrocarbons, but they interpreted a similar parallelism in a little different sense. Assuming the efficiency is entirely controlled by the dissociation reaction $ROH \rightarrow RO\cdot + H\cdot$ and dividing the heat of dissociation into constant σ electronic contribution and variable π electronic contribution $\Delta H_{\pi}(RO-H)$, they derived that in a simple approximation $\Delta H_{\pi}(RO-H)$ is nothing but the energy of the highest occupied level. In this connection a discussion is to be given in the next section on the σ electronic structure and the antioxidantizing efficiency. Pederson's ionic model¹³⁾ also seems to be certified by this parallelism,



but complete one electron transfer would be more difficult than partial electron transfer which is accomplished in the molecular complex.

Delocalization Energy of the Complex. — A more concrete model of the complex, proposed by Russel^{14,15)} and Walling et al.¹⁶⁾, assumes that the peroxy radical will probably approach the inhibitor from the direction perpendicular to the aromatic ring to interact with π electrons on it. If it is true, the delocalization calculation of molecular complexes^{9,10)} will be appropriate. Assuming that the radical stays on the axis which stands from the center of the benzene ring and perpendicular to the ring and that it interacts with six π atomic orbitals on it to the same extent (assumed model of the complex is shown in Fig. 1), we obtain the following stabilization energy of this model by the perturbation treatment, ΔE ,:

$$\Delta E = \left(\sum_i^{occ} - \sum_i^{unocc} \right) \frac{(\sum_r C_{ir})^2}{\lambda_i} \gamma^2 \beta \quad (4)$$

where $\gamma\beta$ is the resonance integral between the half-occupied orbital of peroxide and a π AO on the ring, and \sum_r should cover all AO's on the benzene ring of the compound. Result shown in the fifth column of Table I seems to allow this possibility, too. Charge transfers from the inhibitor to peroxy radical in this model.

Another model of the complex would be such one as illustrated in Fig. 2, in which peroxy radical approaches

oxygen atom of phenol so as to interact with $p\pi$ orbital on it. If peroxy radical is assumed to have one atomic orbital and one electron available to the conjugation with the inhibitor, stabilization energy of the interaction by the second order perturbation treatment is nothing but the superdelocalizability of the oxygen for radical reaction, $S_o^{(R)*}$,¹⁷⁾

$$S_o^{(R)} = \left(\sum_i^{occ} - \sum_i^{unocc} \right) \frac{(C_{io})^2}{\lambda_i} \quad (5)$$

Settling this model Fueno et al.²⁾ found a good linear relationship between logarithm of relative antioxidizing efficiencies by Bolland et al.¹⁾ and superdelocalizability as for several unsubstituted phenols.**

We calculated the superdelocalizability, $S_o^{(R)}$, for this series of compounds, obtaining good parallelism with the potency in each class, as shown in the sixth column of Table I. Thus the model in Fig. 2 may be one of the possible structures of the complex in Eq. 2.

* As the interacting orbital is not the pseudo- π orbital but the half-occupied orbital of peroxy radical, the quantity should be rather named delocalizability instead of superdelocalizability.

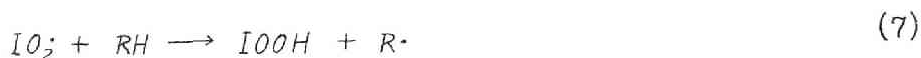
** In the formula of the transferred charge of Fueno's paper a part of the fourth order terms are mixed with the following second order term:¹⁸⁾

$$\Delta q(\text{second order}) = \left(\sum_i^{occ} - \sum_j^{unocc} \right) \frac{(C_{io})^2}{(\lambda_i)^2} f^2$$

Some inhibitor radicals produced by the reaction, Eq.1 or 2, may sometimes initiate a new chain reaction as follows: 19,20)



or



Ingold²¹⁾ has recently proposed to classify the inhibitors into two groups : one is "strong" inhibitor which reacts very rapidly with peroxy radical to break the chain reaction and the other is "efficient" inhibitor whose phenoxy radical produced by the reaction Eq. 1 or 2 is stable enough not to initiate any new chain reaction. Steric hindered inhibitors are "efficient" inhibitors, for their phenoxy radical is protected from reactions to follow.

It would be interesting here to discuss on the difference of potency among classes. In Fig. 3 are plotted calculated indexes against logarithm of potency. In regard to each indexes plots of class A and of class B fall on one line, while those of class C on another line. Compounds of classes A and B are both restricted with bulky tert-butyl group. The same linearity of these two classes seems to suggest that the restriction would be enough by one tert-butyl substitution.

Judging from the models, the indexes calculated seem to represent only the "strength" of inhibitors and, therefore, the difference, which is estimated from Figs. 3 to be of the order of $\log P = 0.4$, should probably be attributed to the difference of the "efficiency".

Total π Electron Density on Oxygen Atom ----- Total π electron density on oxygen atom, q_o , is also calculated and given in the last column of Table I and in Fig. 3c, and here also is got a good parallelism with the antioxidizing potency. As in a radical reaction such as the attack of peroxy radical the total π electron density is no longer the reactivity index, this parallelism would have to be interpreted that the electron density may affect or may be affected by some other quantities. In the next section the total π electron density will be taken as it affects σ electronic structures of the O-H bond.

§3. σ Electronic Structures and Antioxidizing

Activities of Phenols

In this section at first σ molecular orbital calculation on phenol would be presented and then antioxidizing activities would be discussed in connection with the σ electronic structures.

LCAO MO calculation of σ electronic structures of conjugated molecules has been carried out on hydrocarbons,²²⁾ halides²³⁾ and aldehydes²⁴⁾ and parameters of the Coulomb and the resonance integrals of hydrogen and carbon atoms were decided already²²⁾. Parameters for phenolic oxygen are decided as follows: the Coulomb integral of oxygen is settled to be $\alpha_{\sigma} + 0.3\beta_{\sigma}$ in accord with that of aldehyde oxygen, β_{O-O} (one center) = $0.29\beta_{\sigma}$ from the σ MO treatment of alcohols and peroxides²⁵⁾, $\beta_{C-O} = 0.6\beta_{\sigma}$ in accord with the small overlap integral $S(C_{sp^2}-O_p, 1.43\text{\AA}) = 0.37$ in comparison with $S(C_{sp^2}-C_{sp^2}, 1.34\text{\AA}) = 0.77$ and $\beta_{OH} = 0.7\beta_{\sigma}$ also with reference to $S(O_p-H_s, 0.96\text{\AA}) = 0.35$. To make the result more reliable a calculation with another parameter $\beta_{OH} = 1.1\beta_{\sigma}$ is also made.

In Fig. 4 is given the calculated total σ electron density of phenol where we can see clear inductive effect of oxygen atom. Small σ electron density, and therefore large net plus charge on phenolic hydrogen seems to correspond its strong acidity. In Table II are gathered reactivity indexes, delocalizabilities, $D_H^{(N)}$, $D_H^{(E)}$ and $D_H^{(R)}$, for nucleophilic, electrophilic and radical abstractions of phenolic and para hydrogens, corresponding to the model in Fig. 5. Definition of D_H is as follows:²⁹⁾

$$D_H = \sum_i^{\text{all}} (\nu_i - k) \frac{(\sigma_i^H)^2}{\lambda_i^{\sigma}} \quad (8)$$

where ν_i is the number of electrons, on the i th σ MO and k is 0,1,2 according to electrophilic, radical, nucleophilic reactions, respectively, and the energy of the reagent X is assumed to be equal to $\propto \sigma$. In order to agree with experiments that phenolic hydrogen is more labile than p-hydrogen for radical abstraction reactions, if one assumes that the change of the reactivity index will be proportional to the square of β_{OH} as in Fig. 6, $(\beta_{OH})^2$ must be smaller than $0.9(\beta_{\sigma})^2$. Our choice $\beta_{OH} = 0.7\beta_{\sigma}$ would be supported by this result.

Now we are going to discuss relations between σ electronic structures and antioxidizing activities. Experimentally no or small, if any, isotope effects on activities have been observed between substituted phenols and their O-deuterated species²¹⁾ more than between aromatic amines and their N-deuterated derivatives³⁻⁵⁾. It was by this fact that the molecular complex formation has been considered as rate-determining. But there are also some works which reported isotope effects^{26,27)}. Furthermore if the earlier stage of hydrogen abstraction reaction is the transition state of antioxidation, there would naturally be little isotope effects. It would

be worth while to study the possibility of such a mechanism. The delocalizability, whose model (Fig. 5) is composed of a molecule and a reagent weakly interacting to each other and which is derived as a perturbation to a free molecule, would be capable of the measure of this mechanism.

For an attack of peroxy radical a quantity named $D_H^{(R)}$ (0.3) would be more appropriate than $D_H^{(R)}$:

$$D_H^{(R)}(0.3) = \left(\sum_i^{occ} - \sum_i^{unocc} \right) \frac{(C_{iH}^\sigma)^2}{\lambda_i^\sigma - 0.3} \quad (9)$$

This index is derived by the model in Fig. 5 if the Coulomb integral of the orbital X is not equal to α_σ (in the case of $D_H^{(R)}$) but to $\alpha_\sigma + 0.3\beta_\sigma$, the Coulomb integral of oxygen atom. As it is shown in Table III, high reactivity of phenolic oxygen is pointed out also by $D_H^{(R)}(0.3)$. Though ring hydrogens have mutually almost the same reactivities, the order of positions seems to show a slight difference according to the reactivities, $D_H^{(R)}$ or $D_H^{(R)}(0.3)$.

The parallelism of total π electron density on oxygen with the antioxidizing activity, which we showed in the previous section, might be interpreted as follows: total π electron density on oxygen atom increased by methyl and tert-butyl substitutions will necessarily decrease the

electronegativity of the oxygen and make the Coulomb integral of the σ orbitals on oxygen more positive. The change of the Coulomb integral causes changes of the σ electronic structures of phenol, especially at the O-H bond. Putting tentatively the Coulomb integral of oxygen σ orbital equal to $\alpha_\sigma + 0.25\beta_\sigma$, instead of its normal value $\alpha_\sigma + 0.3\beta_\sigma$, we obtained the values of the indexes, $D_H^{(R)}$ and $D_H^{(R)}$ (0.3) shown in Table III. As one can clearly see in the table, for an ordinary radical attack, in which $D_H^{(R)}$ would be the index, the reactivity of phenolic hydrogen would be hardly influenced by the change of total π electron density of oxygen, while for an electronegative radical (such as peroxy radical) attack, in which $D_H^{(R)}$ (0.3) would be the index, the reactivity is much elevated by increased π electron density on oxygen.

In order to see the order of reactivity change the difference of calculated total π electron density in Table I should be translated into the difference of $D_H^{(R)}$ (0.3). The change of the Coulomb integral $\Delta\alpha$ caused by the change of the electron density Δq on the atom is often estimated by the equation:

$$\Delta\alpha = \omega\Delta f \quad (10)$$

where ω is a proportionality constant and would have a value ranging from $0.2\beta\sigma \sim 2\beta\sigma$. * Difference of the total π electron density between the largest and the smallest (phenol) ones in Table I, 0.02, would cause the change of the Coulomb integral $\Delta\alpha = 0.004\beta\sigma \sim 0.04\beta\sigma$. The change of $D_H^{(R)}$ (0.3) would be proportional to the change of the Coulomb integral, the difference of $D_H^{(R)}$ (0.3), 0.1037, for $\Delta\alpha\sigma = 0.05\beta\sigma$ (in Table III) would result $\Delta D_H^{(R)}(0.3) = 0.0083 \sim 0.0830$ between the most reactive and the least reactive compounds. These magnitude of the difference seem to be almost enough to explain practical difference of antioxidizing activity.

* ω is the difference of the Coulomb integral between the two states one of which has one more electron than the other. The difference which is interpreted as that between the ionization potential and the electron affinity of oxygen in its valence state would be about 13 eV.²⁸⁾ As the unit $\beta\sigma$ is estimated to be ca. -7 eV,²³⁾ ω would be ca. $2\beta\sigma$. On the other hand ω value which is often used in π electronic calculation is $0.5\beta\pi \sim 2\beta\pi$ and referring to the ratio $\beta\pi/\beta\sigma \simeq 1/3$,²³⁾ $\omega = 0.2\beta\sigma \sim 0.7\beta\sigma$ seems to be rational.

§4. Discussion

In Sections 2 and 3 we tested several models and their molecular orbital indexes of the rate-determining step of anti-oxidization by substituted phenols. Some molecular complex models were found to be rational, though the problem as to which of them is actually true mechanism of the chain breaking inhibition of autooxidation cannot be settled yet. Another possibility that the earlier stage of hydrogen abstraction reaction may be the rate-determining step does not seem to be abandoned.

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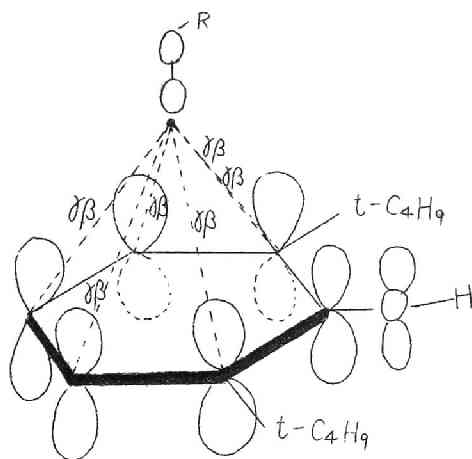


Fig. 1

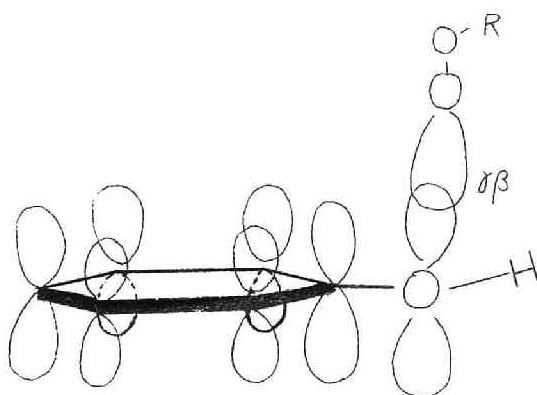


Fig. 2

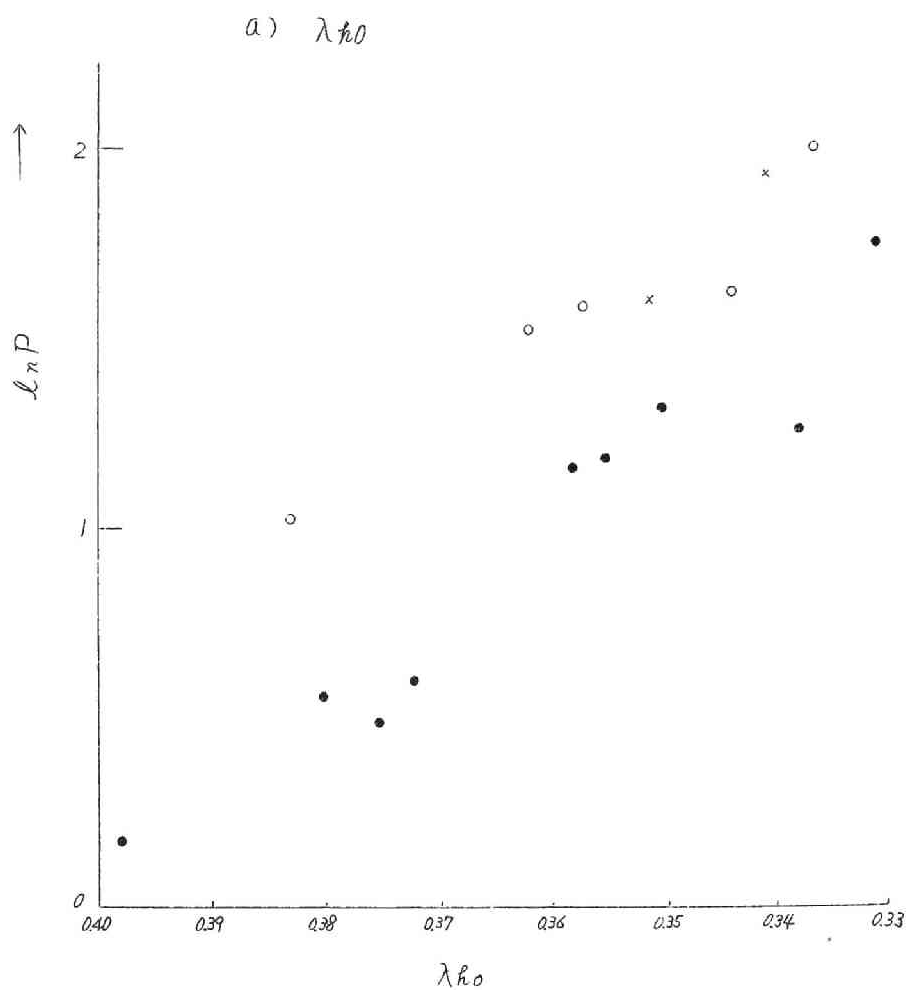
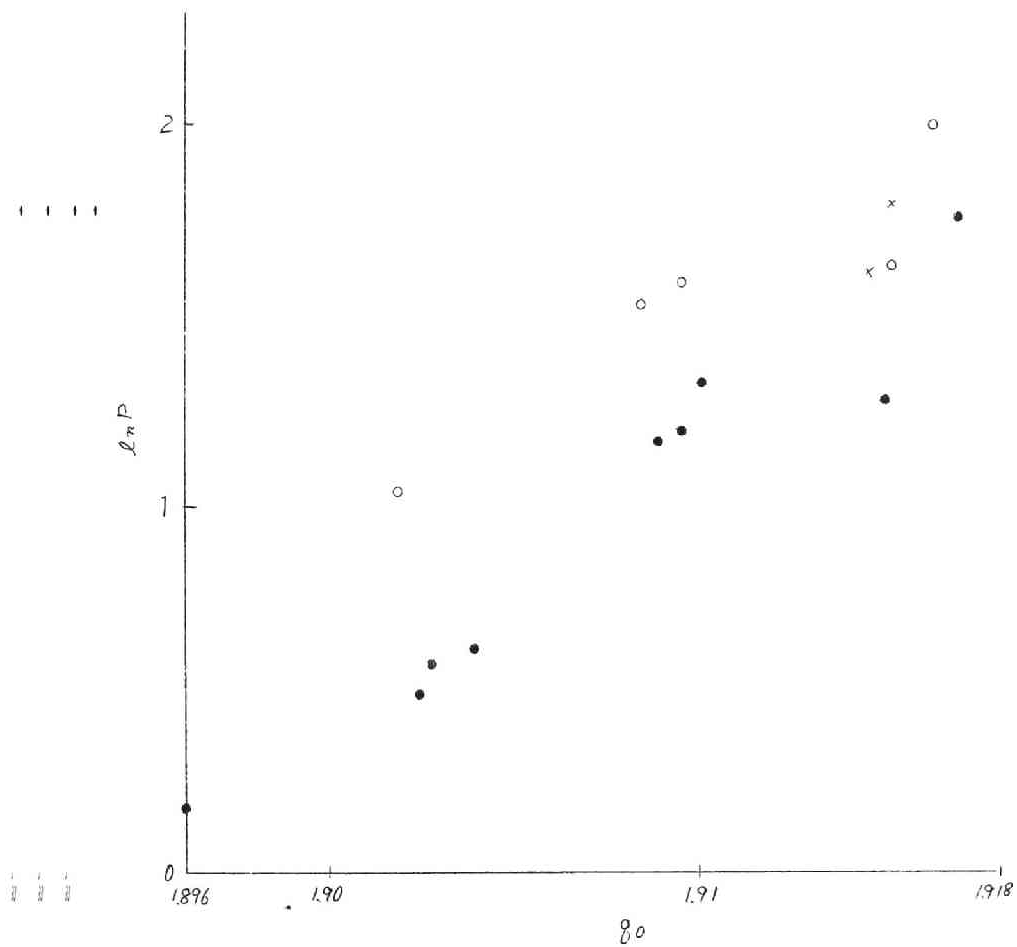
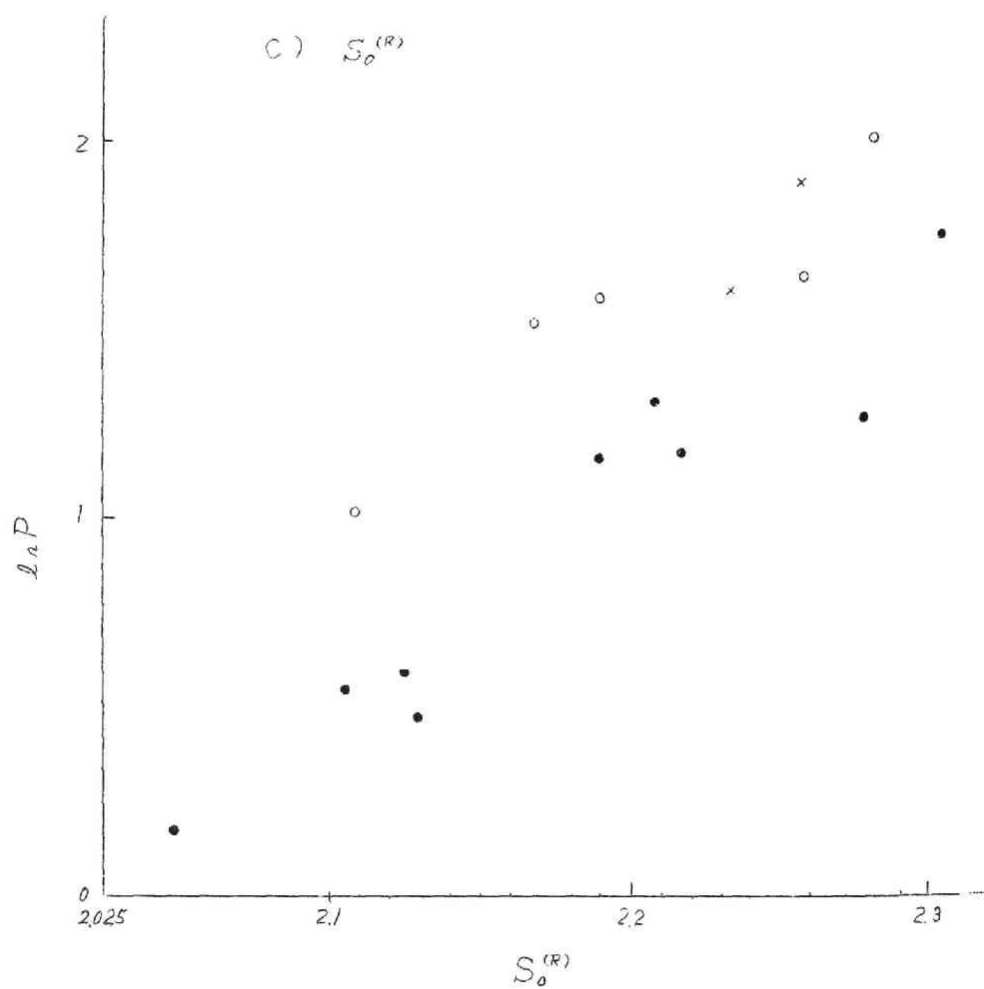


Fig. 3 Linearities between logarithm of antioxidizing potency and reactivity indexes

(x Group A ; o Group B ;
• Group C))

b) 80





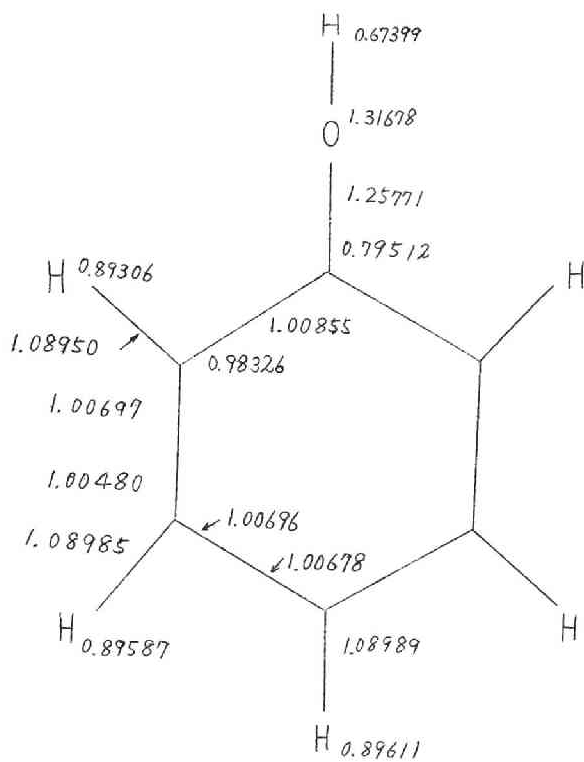


Fig. 4 Total electrin density of phenol
 $(\alpha_o = \alpha_\sigma + 0.3 \beta_\sigma, \beta_{OH} = 0.7 \beta_\sigma)$

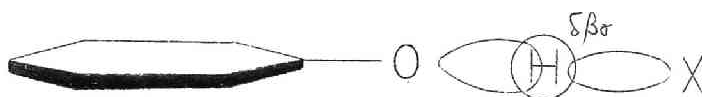


Fig. 5

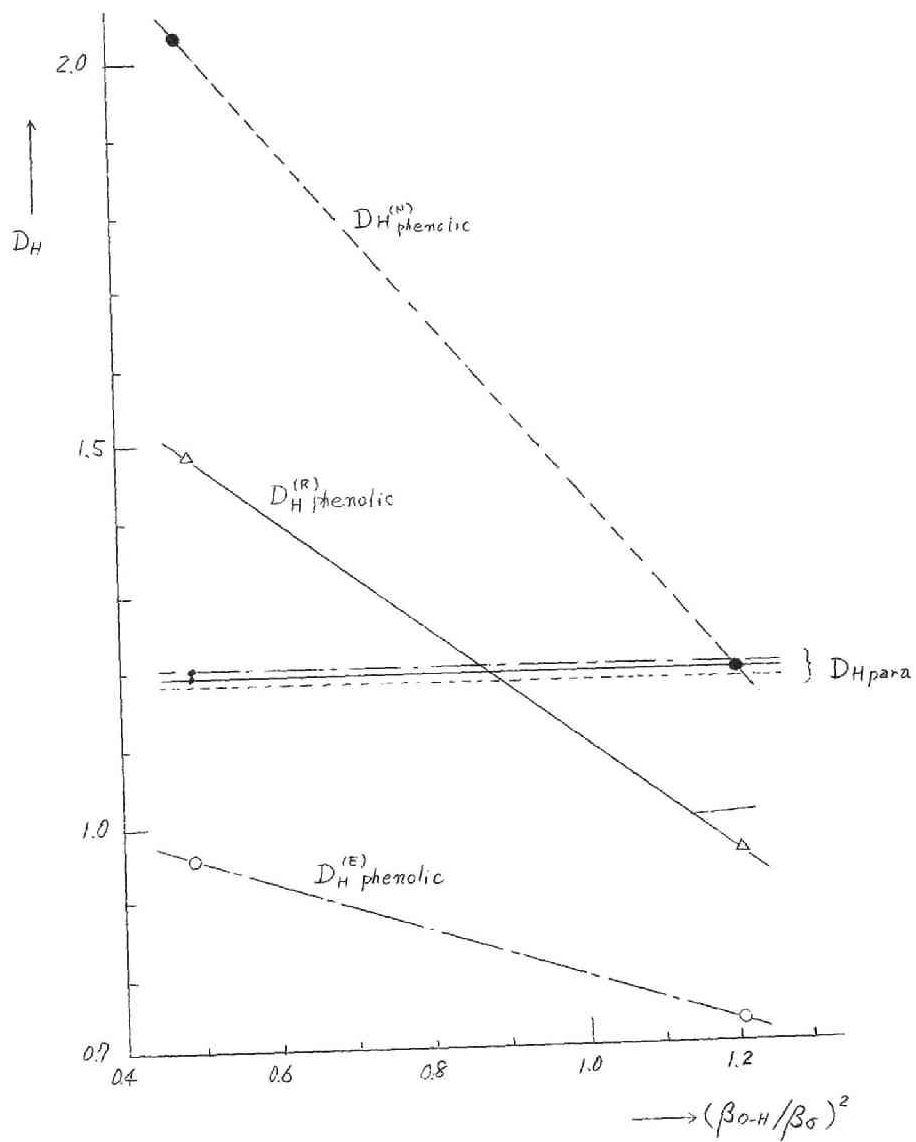


Fig. 6 Crossing of delocalizabilities of phenolic and para hydrogens

Table I. Antioxidizing Potency and π Molecular Orbital Indexes of 2,4,6-Substituted Phenols

Class	Substituents ^{a)} at Position			Relative Molecular Potency (P)	Energy of the Highest Occupied Level ^{b)} λ_{H0}	Stabilization Energy of the Model in Fig.1 $\Delta E, ^c)$	Stabilization Energy in the Model in Fig.2 $S_o^{(R) d)}$	Total π Electron Density on Oxygen ρ_o
	2	4	6					
A	tBu	Me	tBu	76.0	0.343	---	2.257	1.9155
	tBu	tBu	tBu	39.5	.351	---	2.234	1.9145
B	tBu	Me	Me	100.0	.337	3.384	2.281	1.9162
	tBu	tBu	Me	42.5	.344	3.378	2.258	1.9151
	tBu	Me	H	37.5	.357	3.270	2.190	1.9094
	tBu	tBu	H	33.0	.365	3.262	2.168	1.9083
	tBu	H	H	10.5	.383	3.235	2.109	1.9018
C	Me	Me	Me	57.0	.331	---	2.305	1.9169
	Me	Me	H	20.5	.350	---	2.209	1.9100
	Me	tBu	Me	18.5	.338	---	2.282	1.9159
	Me	H	Me	15.0	.355	---	2.215	1.9095
	Me	tBu	H	14.5	.358	---	2.190	1.9089
	H	Me	H	4.0	.372	---	2.125	1.9039
	H	tBu	H	3.5	.380	---	2.106	1.9027
	Me	H	H	3.0	.375	---	2.130	1.9024
	H	H	H	1.5	.398	---	2.049	1.8960

a) Me and tBu stand for methyl and tert-butyl groups, respectively.

b) λ_{H0} is the coefficient of the energy of the highest occupied level:

$$E_{H0} = \alpha + \lambda_{H0}\beta$$

c) In unit of $\gamma^2\beta$.

d) In unit of $\gamma^2\beta$.

Table II Dependency of Delocalizabilities of Hydrogen
on Parameter

β_{OH}		$0.7 \beta\sigma$		$1.1 \beta\sigma$	
Position of Hydrogen		para phenolic		para phenolic	
Total σ Electron Density		0.8961	0.6740	0.8961	0.7852
Delocalizabilities	ρ_H^σ				
	$D_H^{(E)}$	1.2058	0.9529	1.2058	0.7271
	$D_H^{(R)}$	1.1967	1.4949	1.1973	0.9618
	$D_H^{(N)}$	1.1876	2.0369	1.1877	1.1964

Table III Change of Reactivity Indexes of Hydrogen Abstraction.

Δ_0		$\Delta\sigma + 0.3\beta\sigma$		$\Delta\sigma + 0.25\beta\sigma$	
Delocalizability		$D_H^{(R)}$	$D_H^{(R)}(0.3)$	$D_H^{(R)}$	$D_H^{(R)}(0.3)$
Positions	phenolic	1.4949	1.5955	1.4952	1.6992
	ortho	1.2112	1.5050	1.2098	1.5084
	meta	1.1982	1.5041	1.2120	1.5046
	para	1.1967	1.5067	1.1966	1.5069

PART II

THEORETICAL STUDIES

ON PHYSICOCHEMICAL PROPERTIES

Chapter 1

Introduction

Quantum chemistry has offered the theoretical ground on several spectroscopic and other measurements of physicochemical properties of atoms and molecules. The present part of this thesis contains theoretical works on some physicochemical properties of organic compounds, such as dipole moment, coupling constant in pure quadrupole resonance (PQR), half-wave reduction potential, ultra-violet absorption spectrum, coupling constant in electron spin resonance (ESR) spectrum and so forth.

Chapters 2, 3, 4 and 5 are concerned with σ electronic structures of saturated or unsaturated compounds. In Chapter 2 (in press in the Bulletin of the Chemical Society of Japan, 36, No.1 (1963)) is presented a simple molecular orbital calculation of σ electronic structures of conjugated halides such as halogenobenzenes and halogenoethylenes, and general trends of the result is compared with experiences and furthermore observed dipole moments and PQR coupling constants are interpreted in terms of electron distribution. In Chapter 3 (in press in the Bulletin of the Chemical Society of Japan, 36, No.2 (1963)) the energy of the lowest unoccupied

σ electronic level of alkyl halides and conjugated halides are correlated to their half-wave reduction potential and the partial bond order of the level on carbon-halogen bonds to the reduction products, suggesting that in conjugated halides the lowest unoccupied σ level might be near or even lower than the lowest unoccupied π level and that there would be a possibility of observing $\pi \rightarrow \sigma^*$ transition in a range of longer wave length. Chapter 4 (presented at the International Symposium on Molecular Structure and Spectroscopy, Tokyo, September 1962) includes a more strict calculation (an LCAO MO calculation with configuration interaction in which 36 valence electrons are explicitly considered) of the transition energies corresponding to the lowest $\pi \rightarrow \sigma^*$ and the lowest $\pi \rightarrow \pi^*$ transitions. The result is in agreement with the suggestion of the preceding chapter. In Chapter 5 (unpublished) a set of parameters in the simple molecular orbital method by which both σ and π electronic structures of unsaturated hydrocarbons may be calculated unificatively.

Chapter 6 (published in the Bulletin of the Chemical Society of Japan, 32, 853 (1959)) is a short note on electronic spectra and ionization potential of anthracene.

Chapters 7, 8, 9 and 10 are theoretical studies on the

electron spin resonance spectra of organic radicals. In Chapter 7 (published in the Bulletin of the Chemical Society of Japan, 35, 1646 (1962)) presents a new simple molecular orbital method for discussing the difference of π or σ electronic structures between stereo-isomers, and the method is applied to the proton coupling constants in ESR spectra of cis- and trans-terephthalaldehyde anion. Chapter 8 (in press in the Bulletin of the Chemical Society of Japan, 36 (1963)) consists of a valence bond calculation of the proton coupling constants of deformed methylene group adjacent to an odd orbital. The result shows an angular dependency of the proton coupling constants thoroughly different from the current one. Application of the result is made to a radical in irradiated polyethylene. In Chapter 9 (presented at the symposium on ESR, Osaka, 1962) assignment of the observed ESR spectra of irradiated benzene, which is still unestablished experimentally, is performed by valence bond calculations on cyclohexadienyl radical and phenyl radical. Chapter 10 (presented at the symposium on ESR, Osaka, 1962) is concerned with the simpler approximation in the valence bond calculation of spin distribution of hydrocarbon radicals and the result

is used to estimate the coupling constant of some real and some imaginary radicals.

Chapter 2

σ Electronic Structures and Some Physicochemical Properties of Halogenated Conjugated Hydrocarbons

§1. Introduction

Discussions on electronic structures of large organic compounds have been carried out with the molecular orbital and the valence bond methods, almost exclusively on π electronic states of conjugated molecules-----dealing with electronic spectra, chemical reactivities, π dipole moments and so on. In these discussions no regard has been paid to the behaviors of σ electrons as are making an unchangeable framework for π electrons to move on. But some of the physicochemical properties--- σ moments, coupling constants a_{HQ} in PQR spectra, proton shifts in NMR spectra, etc.-- cannot be interpreted theoretically without explicit consideration on the σ electronic structures.

In order to discuss the σ electronic structures of conjugated compounds, the present authors have developed a simple molecular orbital method which had been successfully adopted in the computation of the electronic structures of saturated hydrocarbons and their derivatives,^{1,2,3)} and have published some results of calculation on the σ electrons of

aromatic and olefinic hydrocarbons.⁴⁾ In this chapter a numerical calculation is performed on the σ electronic structures of halogenated olefins and benzenes, and on this basis eqQ of halogens and dipole moments of these compounds are discussed.

It would be interesting to compare the calculated results on conjugated halides in this chapter to those on saturated halides in Refs. 2 and 3.

§2. Method of Calculation and Evaluation of Parameters

The method of the theoretical calculation of σ electronic structures of conjugated systems was explained in detail in Ref. 4. In this chapter, therefore, it would be repeated only briefly. Molecular orbitals are linear combinations of all σ atomic orbitals (LCAO) of all consisting atoms--- sp^2 hybridized orbitals of carbons, 1s orbitals of hydrogens and σ atomic orbitals of halogens. And electronic interactions and overlap integrals are thoroughly neglected. Parameters of the Coulomb and the resonance integrals employed are given in Table I. Those for carbon atoms and for hydrogen atoms are the same as were given in Ref. 4. Coulomb integrals for halogen atoms are settled so as to fit Mulliken's electro-

negativity scale and to be consistent with the integrals in saturated compounds, and resonance integrals between carbon and hydrogen are proportionated to the overlap integrals of the bonds.

Effects of variation of parameters and those of neglecting overlap integrals would be discussed in following paragraphs.

§3. Results of Calculation and Their General Properties

A few examples of the results of our calculation are shown in Tables II, III and IV and Figs. 1, 2, 3 and 4. On inspection of the tables and the figures general properties of these results for halogenated conjugated systems may be summarised as follows:

(1) As is seen in Tables I and II and Fig. 1, each orbital has a large distribution on certain two atomic orbitals which are constructing a bond. This tendency seems to reflect the localized nature of σ electrons.

(2) The lowest unoccupied σ orbital of halides lies much lower than that of mother hydrocarbons and it is localized on carbon-halogen bonds with negative and large (in magnitude) bond order. And the lowering of the level becomes more and more notable with increased number of halogen atoms. This result comes from the electronegativity of the halogen

atoms and the small overlap (the small absolute value of the resonance integral) between the carbon and the halogen.

(3) Electronegativity of the halogen atoms make them attract a considerable amount of electron density to the carbon-halogen (C-X) bonds from other bonds near-by, so that the sum of σ charge density on the bond (the σ bond density) exceeds 2 and the net charge on the bond becomes negative.

(4) Owing to the polarity of a C-X bond, X being negative and C being positive, the similar but weakened polarity is caused in adjacent C-C bonds and it is transmitted to farther bonds with rapid decrement.

Results (3) and (4) seem to correspond to the so-called inductive effect in organic chemistry.

§4. Effects of Parameters

In order to see effects of parameters on the results, some calculations on various compounds are carried out with varied parameters; a few example is shown in Table V and VI. For the sake of brevity, only summary of calculated results will be reported. Change in the Coulomb integral of chlorine atoms causes change in their σ electron density, and the bond moment of the C-Cl bond is well explained with its value near 0.3 as is adopted or less, though influence is little on

qualitative results of calculation.

§5. Effects of Overlap Integrals

In σ electron systems where neighboring atomic orbitals are mutually overlapping deep, the neglect of the overlap integrals might lead to an erroneous conclusion even in a qualitative sense. So some computations are performed with inclusion of overlap integrals between adjacent atoms, which are settled as follows:

$$S_{CH} = 0.72$$

$$S_{CC} = 0.77$$

$$S_{CCl} = 0.46$$

Results with respect to ethylene, 1,2-dichloroethylene, tetrachloroethylene, benzene and p-dichlorobenzene, as shown in Table VII and Figs. 5 and 6, indicate that energy levels with overlap included are almost completely parallel to those with overlap neglected and that occupied levels of the former come near to $\alpha\sigma$ and unoccupied levels flee from $\alpha\sigma$. As for the σ electron density, from Fig. 6, those on similar atomic orbitals on similar bonds (for instance, carbons' AO's on C-Cl bond as are expressed by C_{Cl} in the figure) very parallel with each other, leading also to an unvaried qualitative conclusion in both calculations.

§6. Dipole Moments

Dipole moment of conjugated compounds is composed of σ moment and π moment. With only π moment have been concerned most of the theoretical works till now, and in those cases σ moment would be empirically estimated on the basis of bond moments which are assumed to be constant in a series of compounds. In this paragraph σ moment of each compound is evaluated by the use of σ electron distribution given in the tables and the figures. In the evaluation all the bond angles are assumed to be 120° , and C-Cl bond length to be 1.70\AA , C-H 1.08\AA , C-C(aromatic) 1.40\AA and C-C(olefinic) 1.34\AA , and the displacement of the center of the charge distribution is taken into account by 0.46\AA in a sp^2 hybridized orbital of carbon and by 0.44\AA in a σ orbital (the s character of 15% is tentatively assumed) of chlorine.

Obtained σ moments are tabulated in Tables VIII and IX, together with π moments calculated in the simple LCAO MO approximation with parameters $\alpha_{Cl}^\pi = \alpha_\pi + 1.8\beta_\pi$ and $\alpha_C^\pi = \alpha_\pi + 0.18\beta_\pi$ and $\beta_{C-Cl} = 0.6\beta_\pi$ where α_π and β_π is the standard Coulomb and the standard resonance integrals in π electron systems and with calculated total moments in comparison with the observed dipole moments.

Generally speaking, calculated moments are larger than

observed ones, which would be attributed to the choice of parameters and also to neglecting σ overlaps. But a σ moment calculated does not seem to be a simple vector sum of bond moments. A part of the so-called ortho effects---deviation from the additivity of bond moments in ortho disubstituted compounds---would be understood on the basis of this result. But the extremely small moment of trichloroethylene cannot be explained, probably due to the roughness of the electronic repulsions between the neighboring polar groups. On these problems a few theoretical papers would be published in the near future.⁵⁾

§7. Coupling Constant of Halogen in Pure Quadropole Resonance Spectra

In chlorides, bromides and iodides are observed the coupling constants, eqQ , of halogen nuclei in the pure nuclear quadropole resonance (PQR) spectroscopy. In conjugated chlorides it is connected to σ electron density, q_{cl}^{σ} , and π electron density, q_{cl}^{π} , on the chlorine atom by the following equation:

$$eqQ = \left(\frac{q_{cl}^{\pi} + 2}{2} - q_{cl}^{\sigma} \right) eqQ_{atom} \quad (1)$$

where eqQ_{atom} is the coupling constant of an atomic chlorine

and is set to be 109.7 Mc. In Eq. 1 the orbital of chlorine is assumed to be a pure p orbital. If the s character of the orbital considered to be s %, eqQ is given by Eq. 2 instead of Eq. 1.

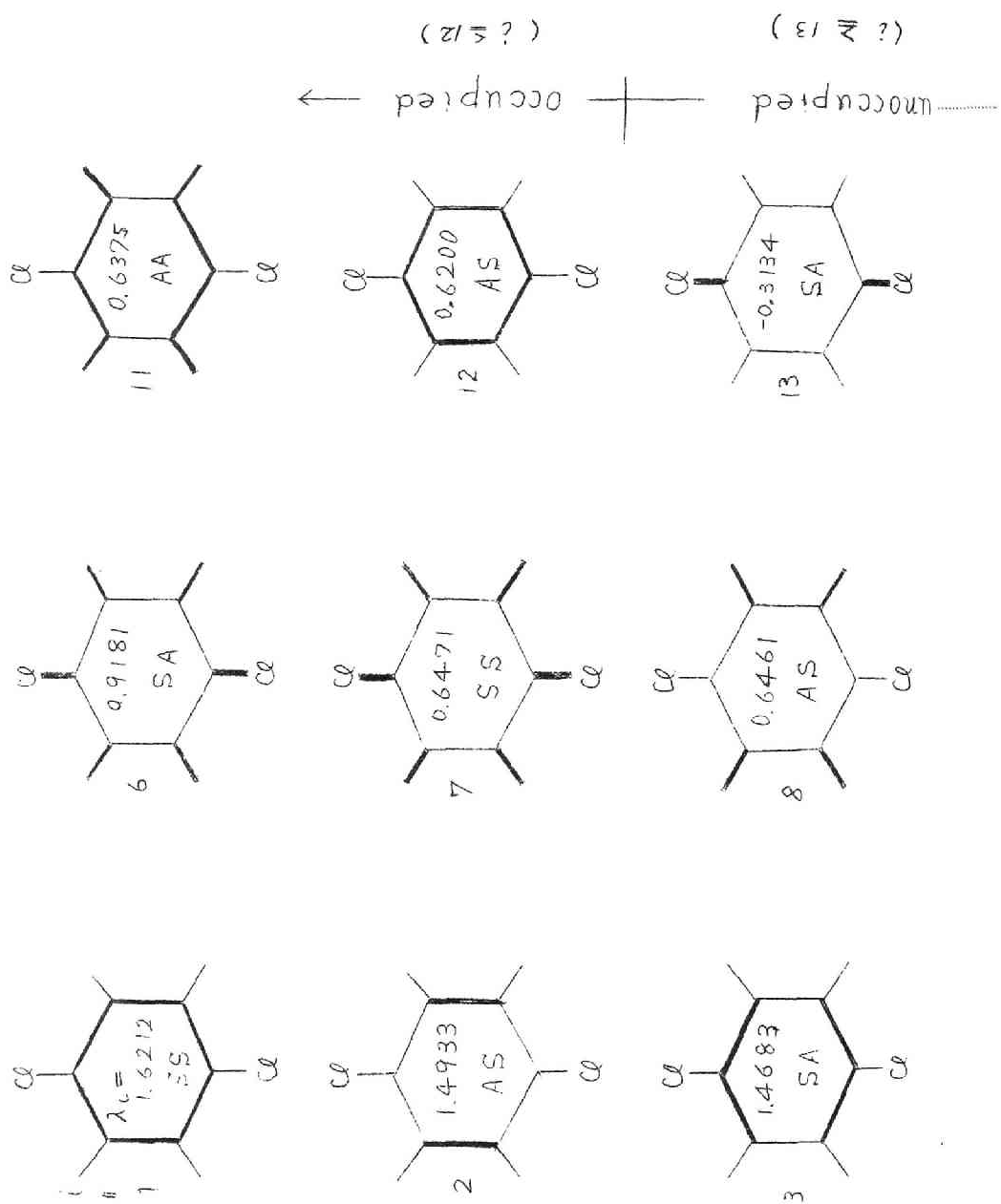
$$eqQ = \left[\frac{\rho_{Cl}^{\pi} + 2}{2} - \rho_{Cl}^{\sigma} - \frac{s}{100} (2 - \rho_{Cl}^{\sigma}) \right] eqQ_{atom} \quad (2)$$

By adopting the π and the σ electron densities calculated in previous paragraphs to Eq. 1, the values of eqQ are obtained, as is shown in Tables X and XI; parallelism with experimental values seems to be enough.

Difference of the calculated coupling constants among chlorobenzenes is unexpectedly small. As the coupling constant of these compounds was experimentally determined from the resonance spectra in the solid state, a part of the discrepancy would be attributed to effects of crystal fields which in some other cases might change the constant by 0.8 Mc.⁶⁾ Another part, however, is probably due to the crudeness of our approximation in calculating molecular orbitals. On the approximation of this calculation some discussions have been made by the present authors.⁵⁾

References

- 1) K. Fukui, H. Kato and T. Yonezawa, Bull. Chem. Soc. Japan, 34, 442, 1111 (1961).
- 2) K. Fukui, T. Yonezawa, H. Kato, Progress Reports on Electronic Processes in Chemistry. 2, 55 (1961).
- 3) T. Yonezawa, H. Kato, H. Saito and K. Fukui, Bull. Chem. Soc. Japan, 35, 1814 (1962).
- 4) K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, Bull. Chem. Soc. Japan, 35, 38 (1962).
- 5) K. Morokuma, and K. Fukui, presented at the 15th annual meeting of the Chemical Society Japan, Kyoto, 1962.
See also Part II Chapter 7 of this thesis.
- 6) In the case of chloroalkanes. H. O. Hooper and P. J. Bray, J. Chem. Phys. 22, 334 (1960).



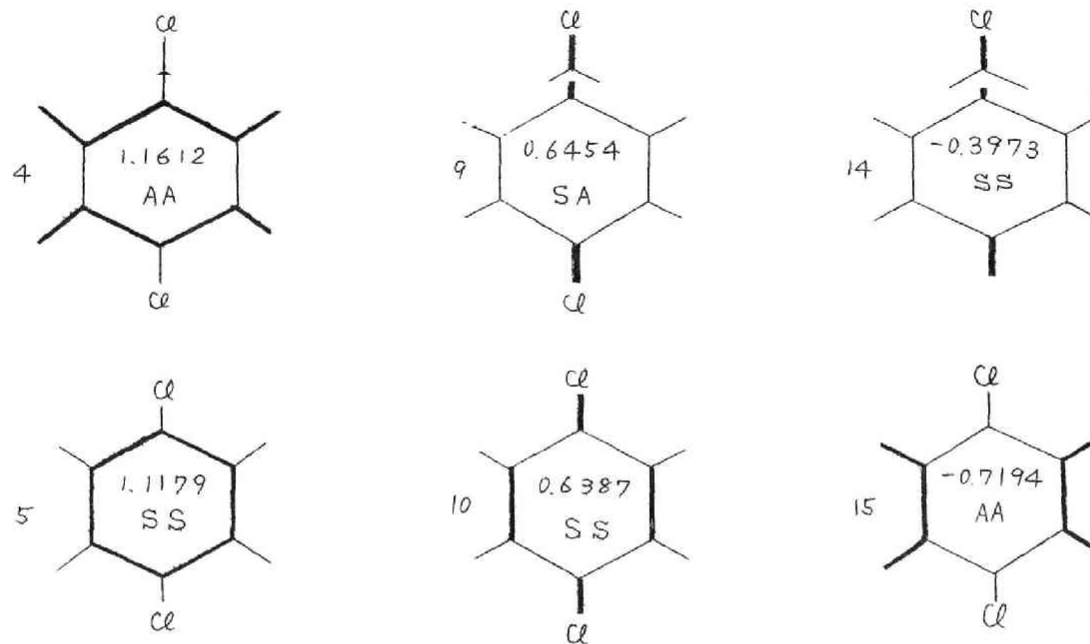
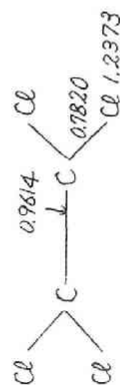
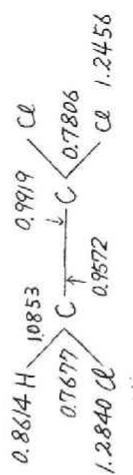
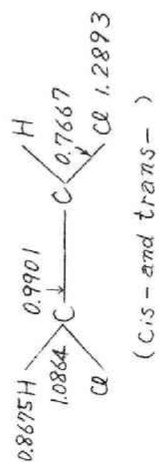
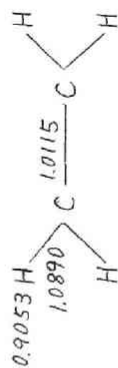
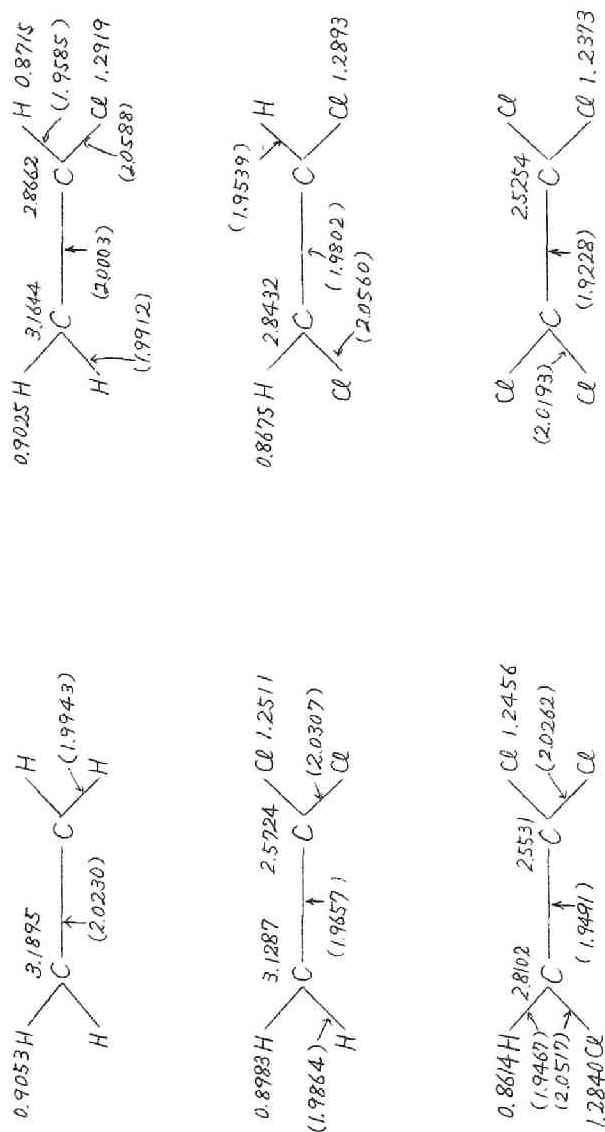


Fig. 1 The σ electron distribution and the energy λ_i of some MO's in p-dichlorobenzene
(Thick lines denote the most densely populated bonds)

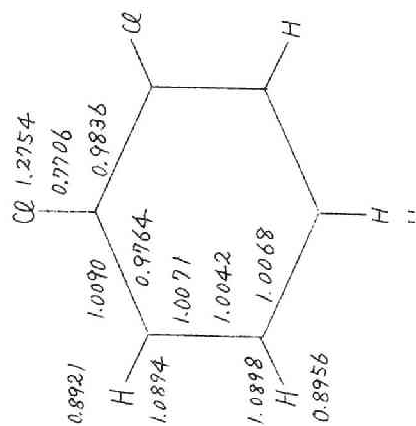
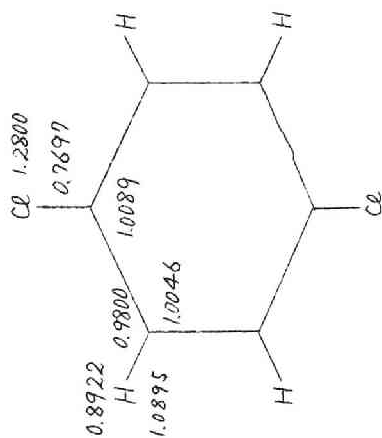
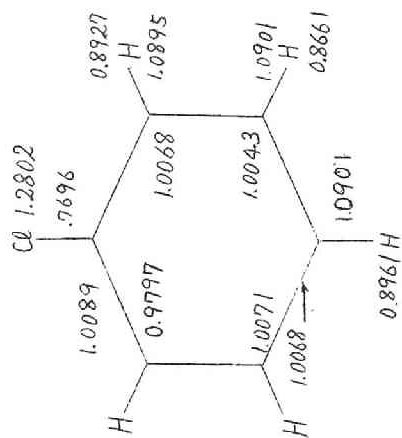
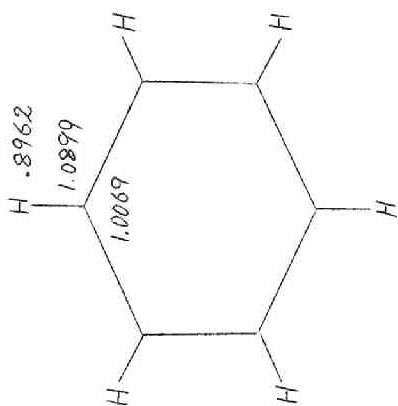


(a) σ Electron density on each A0



(b) Total σ electron density on each atom and bond σ density (in parentheses)

Fig. 2 Electron distributions of ethylene and chloroethylenes



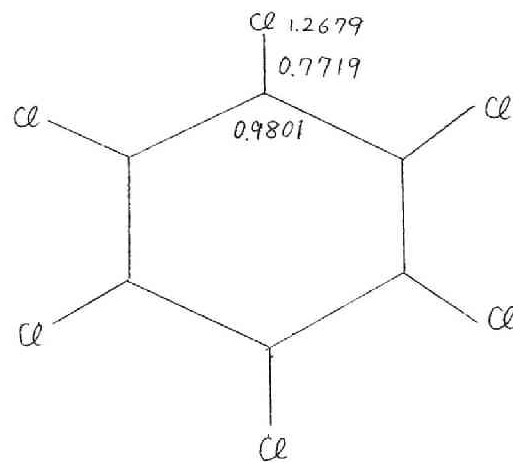
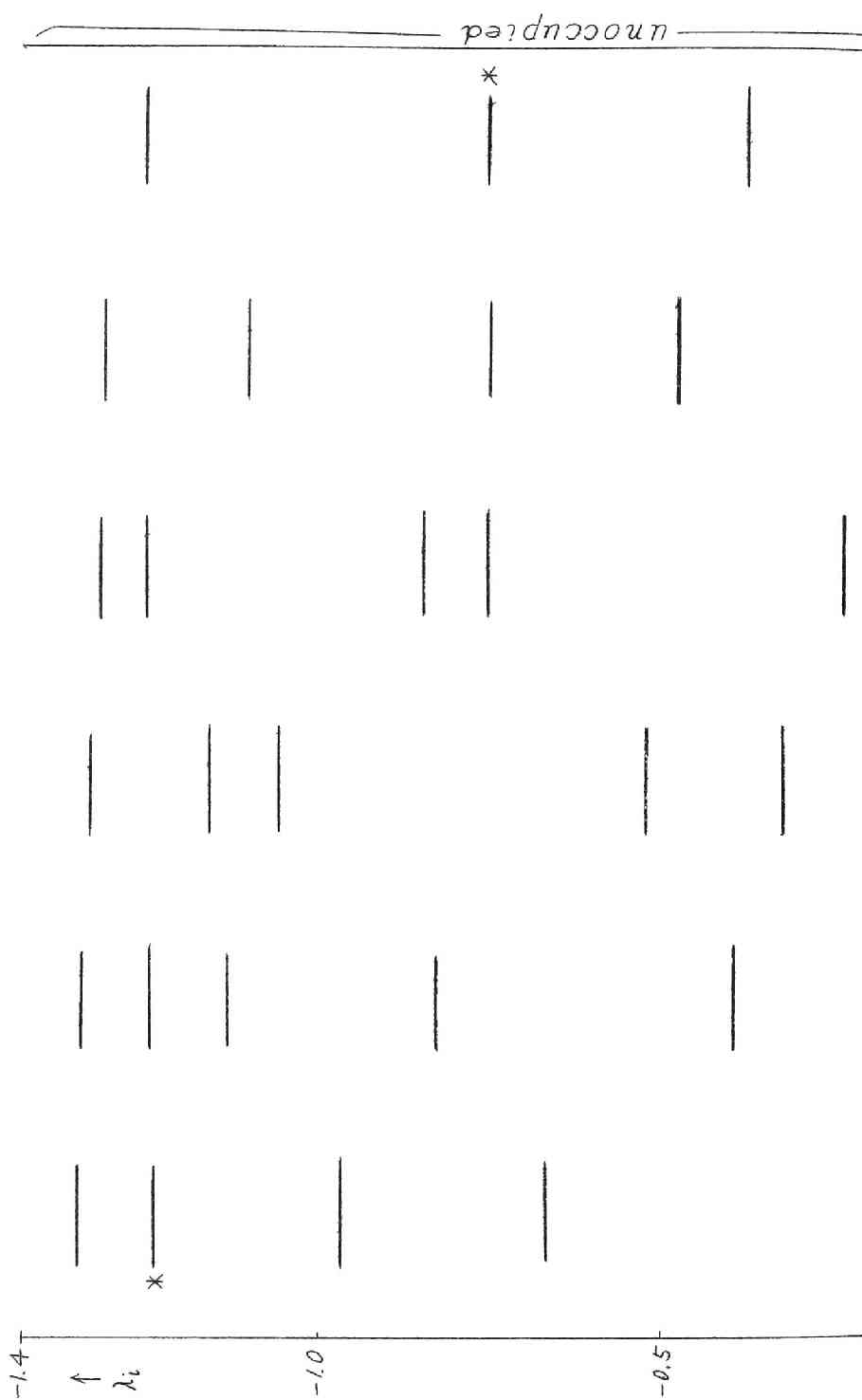


Fig. 3 Total σ electron density of benzene and chlorobenzenes



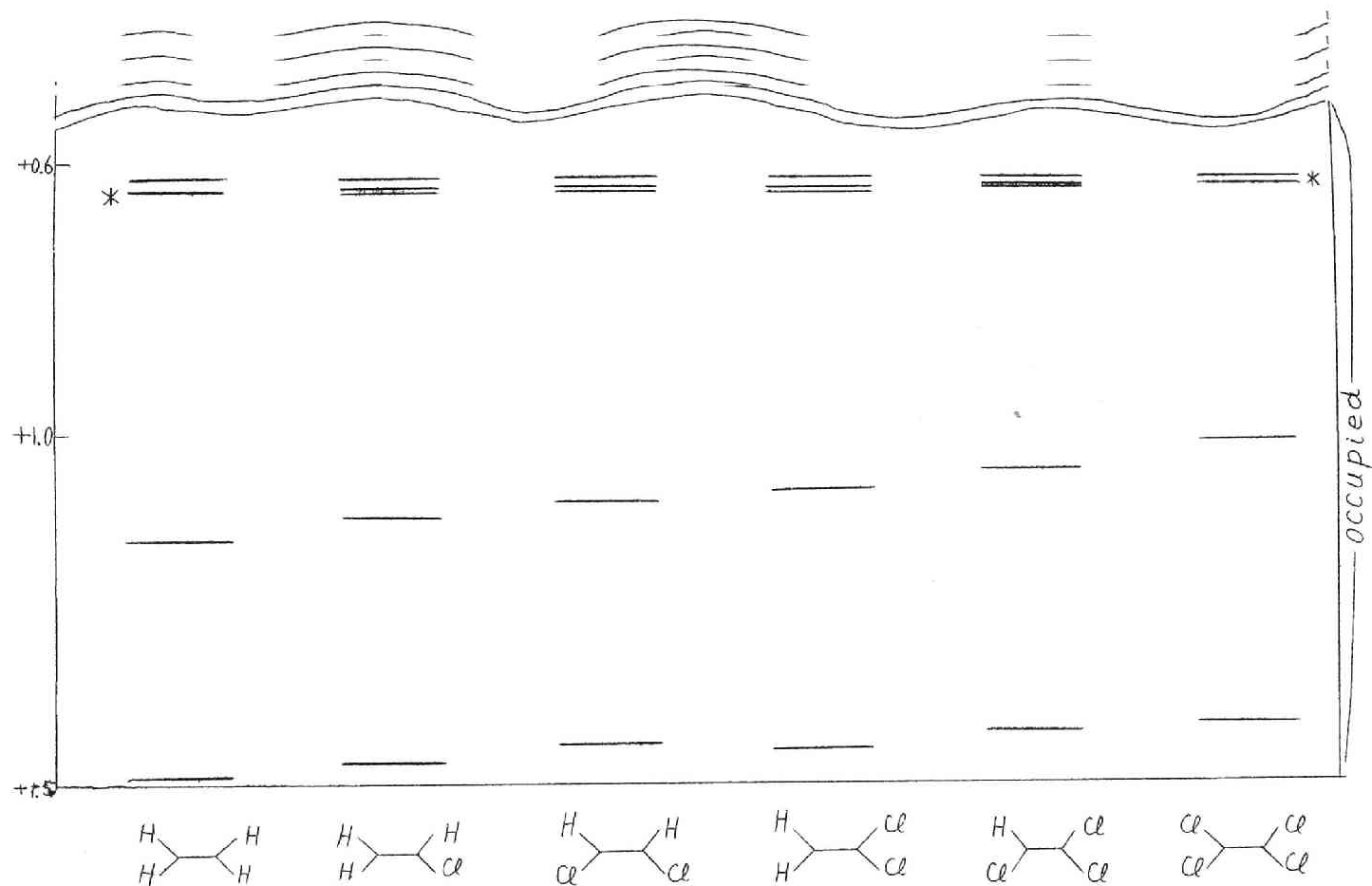
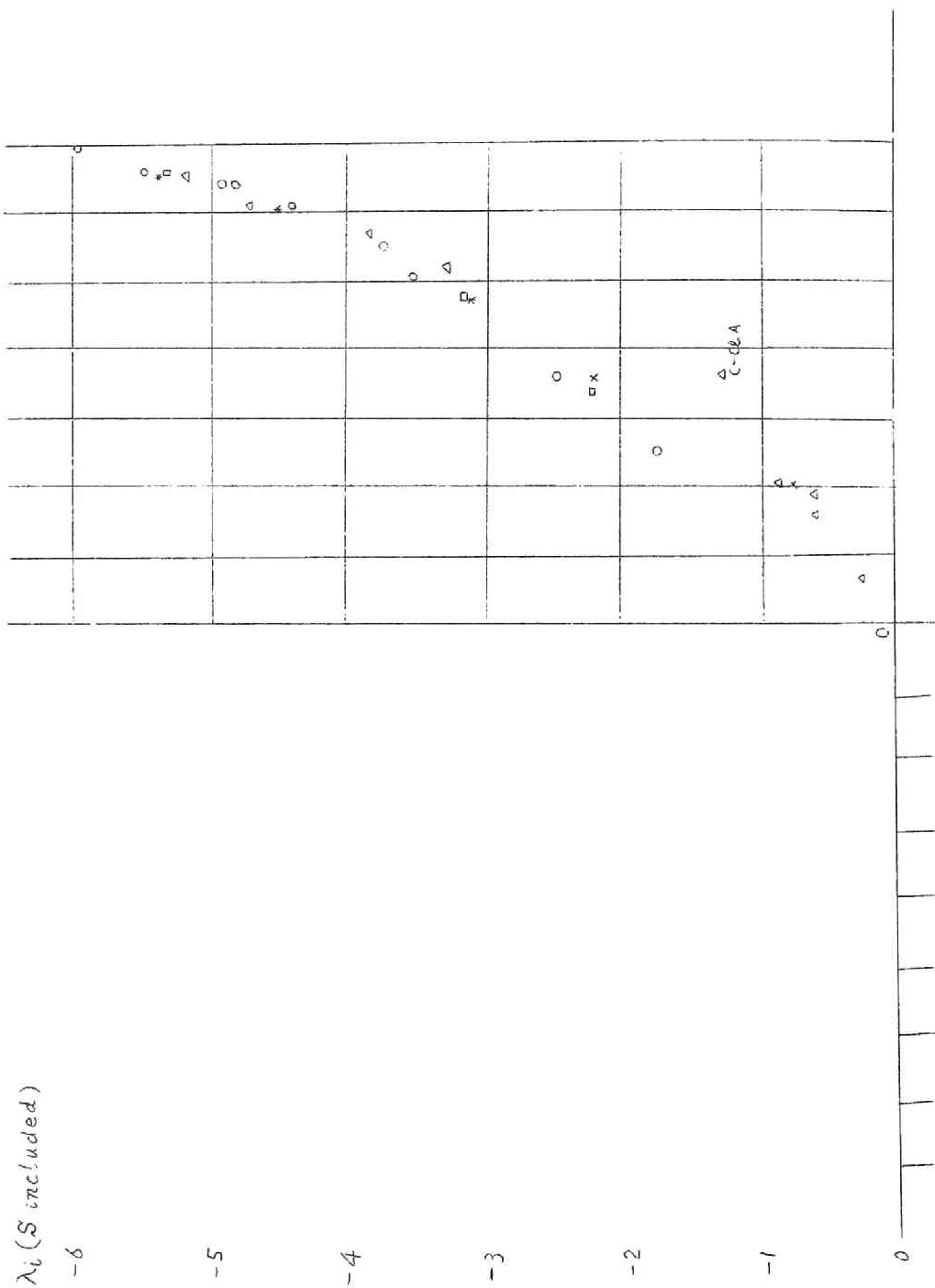


Fig. 4 Energy levels of ethylene and chloroethylenes
(*:doubly degenerate level)



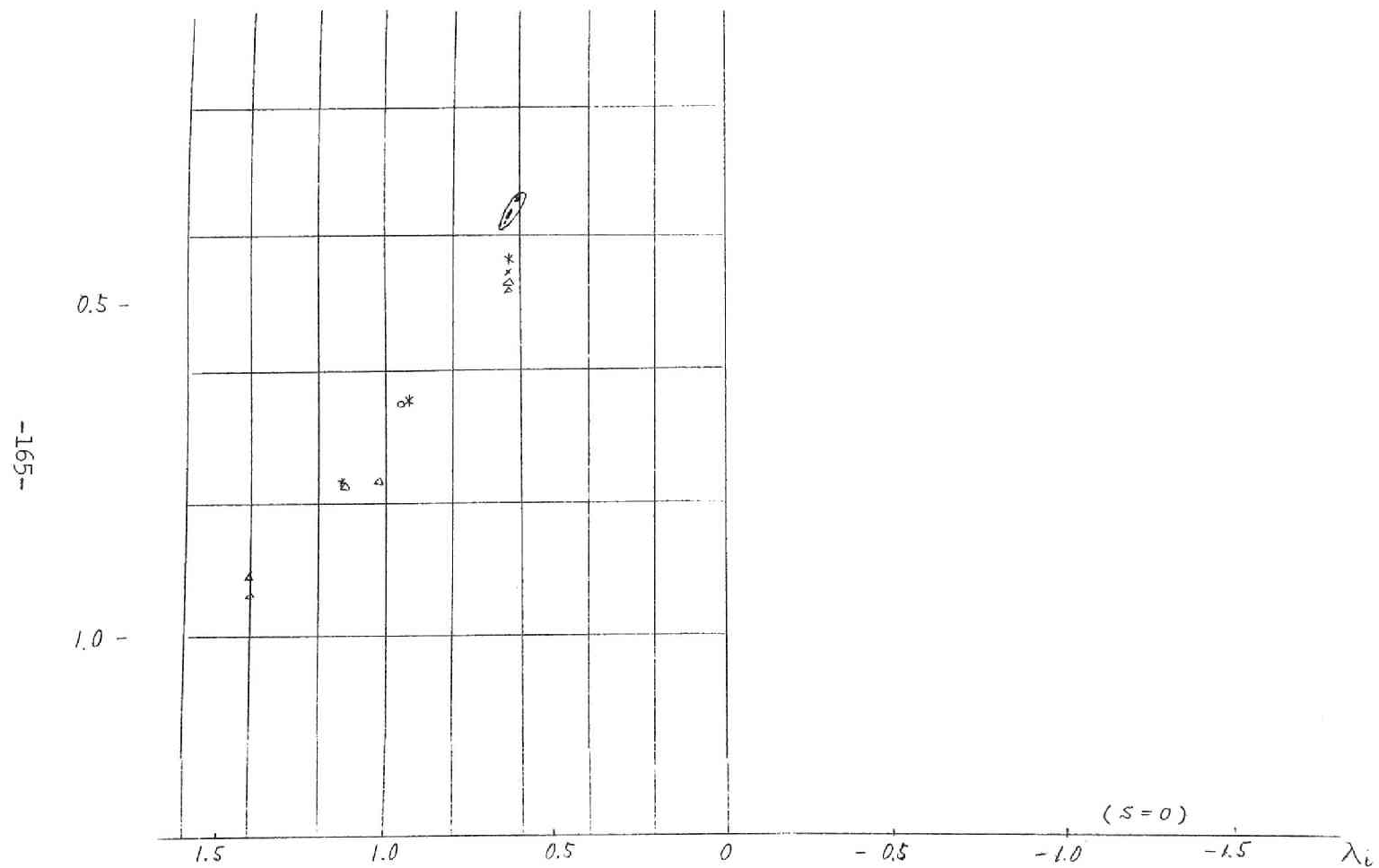


Fig.5 Energy levels with overlap included and neglected

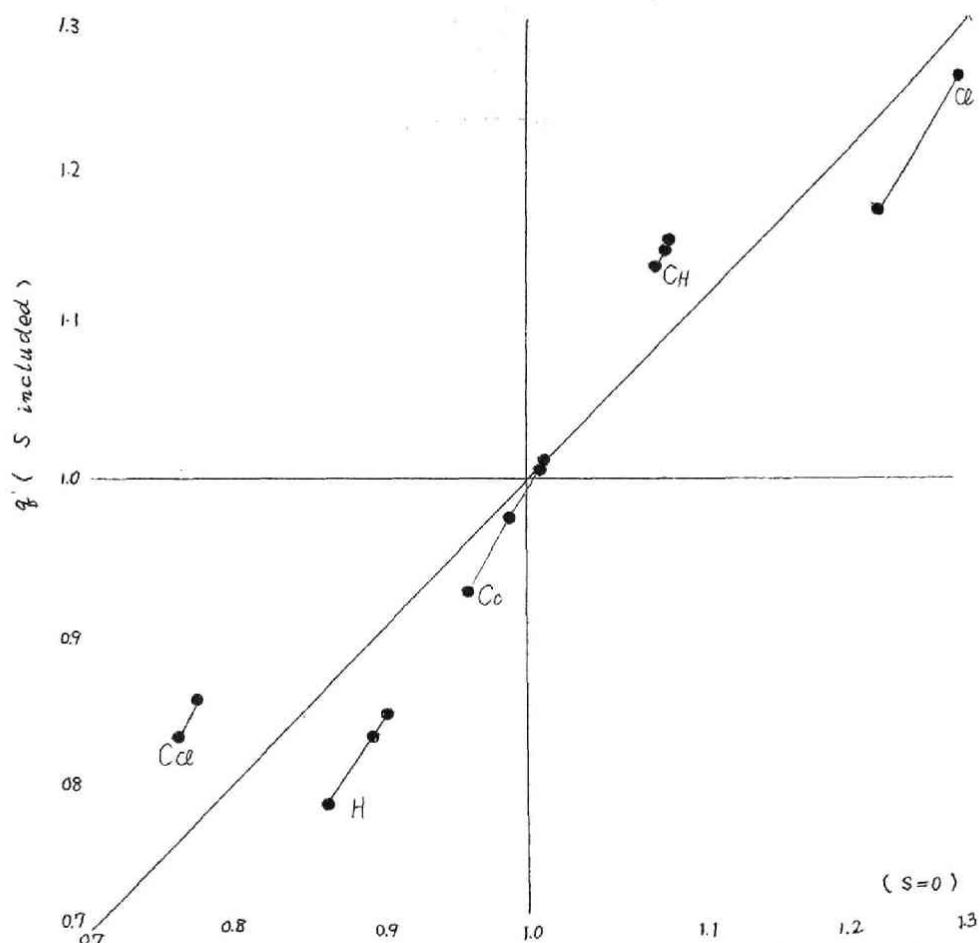


Fig. 6 Total σ electron density on each kind of atoms
(CH , for example, denotes the carbon atom in a
CH bond)

Table I Parameters of Coulomb and Resonance Integrals
of σ AO's

Coulomb Integral :	a_{rr}^x	Resonance Integral : a_{rs}^{**}	1
C_{sp^2}	0	$C_{sp^2-C_{sp^2}}(\sigma \text{ bonding})$ (on the same carbon) $m \equiv 0.38$	
H	-0.2	C_{sp^2-H}	0.94
F	0.7	C_{sp^2-F}	0.45
Cl	0.3	C_{sp^2-Cl}	0.6
Br	0.25	C_{sp^2-Br}	0.5
I	0.2	C_{sp^2-I}	0.45

* Coulomb integral α_r is expressed as follows

$$\alpha_r = \alpha + a_{rr}\beta$$

where α and β are the standard Coulomb and the
standard resonance integrals in sp^2 system.

** Resonance integral β_{rs} is expressed as follows

$$\beta_{rs} = a_{rs}\beta$$

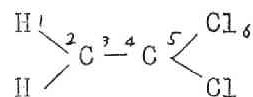
Table II Calculated σ Electronic Structure of Vinylidene Chloride

Symmetry*	Energy** λ_i	Electron Distribution on Each AO***					
		H ₁	C ₂	C ₃	C ₄	C ₅	Cl ₆
occupied	10 S	.05763	.07558	.36551	.31672	.02242	.00325
	9 A	.22617	.27383	0	0	0	0
	8 S	.24699	.10654	.04037	.16999	.03205	.00924
	7 A	0	0	0	0	.37325	.12675
	6 S	.02004	.00002	.11787	.00668	.18247	.23519
	5 S	+0.6387	.04673	.20443	.20529	.04585	.14386
unoccupied	4 A	0	0	0	0	.12675	.37325
	3 A	.27383	.22617	0	0	0	0
	2 S	.07398	.13858	.00037	.06859	.15991	.09305
	1 S	.04266	.13255	.27145	.23274	.05729	.01541

* Symmetry about the C-C axis.

** λ_i is the coefficient in $\varepsilon_i = \alpha + \lambda_i \beta$, where ε_i is the i th molecular orbital energy.

*** Nomenclature of AO's



And $(C_{1r})^2$ is given in the table.

Table III Calculated σ Electronic Structure of
Tetrachloroethylene

Symmetry	Energy λ_i	Electron Distribution on Each AO**			
		Cl ₁	C ₂	C ₃	
unoccupied	A	-1.2131	.00523	.03326	.42302
	AA	-0.7296*	.12675	.37325	0
	S	-0.3690	.10267	.12766	.03934
	A	-0.1286	.14669	.07484	.05693
occupied	S	+0.6395	.12307	.03939	.17506
	AA	+0.6496*	.37325	.12675	0
	A	+1.0217	.09808	.14189	.02005
	S	+1.4096	.02425	.08295	.28560

* Doubly degenerate orbital being localized on C-Cl bonds.

** Nomenclature of AO's:

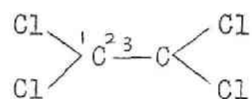


Table IV Calculated σ Electronic Structure of
Hexachlorobenzene

		Symmetry	Energy	Electron Distribution on Each AO			
		j	xy	λ_j	C1	C2	C3
unoccupied		24	AA	-1.38000	0	0	.08333
		22,23	SA,AS	-1.27825	.00209	.01448	.15838
		20,21	SS,AA	-1.08869	.01299	.06956	.12539
		19	SA	-1.01172	.01128	.05391	.05074
		18	SS	-0.56479	.05150	.10699	.00408
		16,17	SA,AS	-0.52114	.10496	.19659	.01589
		14,15	SS,AA	-0.34699	.11312	.13154	.04434
		13	SA	-0.15872	.07009	.04097	.02780
occupied		12	AS	+0.62000	0	0	.08333
		10,11	SS,AA	+0.63931	.16148	.05164	.06011
		8,9	SA,AS	+0.64524	.21223	.07026	.02542
		7	SS	+0.64622	.11026	.03671	.00985
		6	SA	+0.85044	.08529	.07178	.00479
		4,5	SS,AA	+1.09637	.04575	.08059	.10350
		2,3	SA,AS	+1.45415	.01405	.05200	.13364
		1	SS	+1.59857	.00490	.02296	.06940

Table V Variation of Parameters (1)

1,2-Dichloroethylene

a_{cl}	ρ_{cl}	ρ_H
0.25	1.2488	0.8721
0.28	1.2733	0.8692
0.30	1.2893	0.8675

Vinyl Chloride

a_{cl}	ρ_{cl}	ρ_H	ρ_{H_2}
0.25	1.2522	0.8754	0.9028
0.28	1.2765	0.8730	0.9027
0.30	1.2929	0.8715	0.9025
0.32	1.3088	0.8699	0.9024

Table VI Variation of Parameters (2)

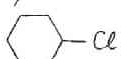
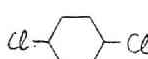
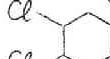
a_{cl}	m	ρ_{cl}		
				
0.6	0.38	1.2802	1.2800	1.2754
0.6	0.42	1.2914	1.2910	1.2851
0.6	0.45	1.3010	1.3005	1.2935
0.8	0.42	1.2206	1.2205	---

Table VII Electron Distribution of Tetrachloroethylene
with Overlap Included

Energy λ_i	Electron Distribution(a)**					Electron Distribution(b)***		
	Cl ₁	C ₂ Cl ₁	C ₂	C ₃	C ₃ C ₄	Cl ₁	C ₂	C ₃
+0.42935	.10799	.03193	.01115	.11179	.17216	.12395	.02712	.19787
+0.47204*	.30954	.12796	.06250	0	0	.37352	.12648	0
+0.76116	.03989	.06772	.13586	.05683	-.08752	.07375	.16972	.01307
+0.90885	.00814	.02505	.09111	.14205	.21875	.02066	.10363	.25143
\bar{v}	.93109	.50531	.60123	.62134	.60678	1.18375	.85389	.92473

* Doubly degenerate orbital

** Electron distribution on the atom A is $(C_{iA})^2$, while on the bond AB it is
calculated as $2C_{iA} C_{iB} S_{AB}$.

*** In this calculation distribution on the bond AB is divided by two and added to
those on the atom A and on the B.

Table VIII Dipole Moments of Chloroethylenes
(In Unit of Debye)

Substituent	Calculated			Observed
	σ Moment	π Moment	Total Moment	
Cl	1.84	0.36	1.47	1.44
1,2-di-Cl(cis)	3.20	0.65	2.55	1.74
1,1-di-Cl	1.81	0.34	1.47	1.30
tri-Cl	1.84	0.37	1.47	0.94

Table IX Dipole Moments of Chlorobenzenes
(In Unit of Debye)

Substituent	Calculated			Observed
	σ Moment	π Moment	Total Moment	
Cl	1.69	0.31	1.39	1.57
o-di-Cl	2.96	0.54	2.41	2.25

Table X Chlorine Coupling Constants in PQR of Chloroethylenes

Substituent	Calculated			Observed
	q_{α}^{π}	q_{α}^{σ}	$eq Q$	$eq Q$
Cl	1.955	1.298	75.1 ^{Mc}	67.2 ^{Mc}
1,2-di-Cl	1.955	1.289	75.6	70.2(gas) 70.0(cis) 71.2(trans)
1,1-di-Cl	1.956	1.251	79.8	78.7(gas)
tri-Cl	1.956	1.246	80.3	—
	1.954	1.284	76.0	—
tetra-Cl	1.955	1.237	81.3	77.2

Table XI Chlorine Coupling Constants in PQR of Chlorobenzenes

Substituent	Calculated			Observed ^{a)}
	q_{α}^{π}	q_{α}^{σ}	$eq Q$	$eq Q$
Cl	1.96200	1.28022	76.9 ^{Mc}	69.2 ^{Mc}
p-di-Cl	1.96188	1.28000	76.9	69.6
o-di-Cl	1.96166	1.27540	77.4	71.5
hexa-Cl	1.96126	1.26793	78.2	76.8

a) P. J. Bray, R. G. Barnes and R. Bersohn, J. Chem. Phys., 25, 813 (1956).

Chapter 3

Polarographic Reduction and Electronic Structures of Organic Halides

§1. Introduction

In the last fifteen years polarographic reduction of a number of conjugated hydrocarbons has been extensively studied both experimentally and theoretically, and their pH-independent reversible half-wave reduction potentials, $E_{1/2}$, were found to be linearly related to the energy, $\varepsilon_{\ell\nu}^\pi$, of their lowest unoccupied π orbital,^{1,2)} the energy which would be needed in order to bring an electron to the orbital, as follows:

$$-E_{1/2} = \lambda_{\ell\nu}^\pi \beta_\pi + C \quad (1)$$

where $\lambda_{\ell\nu}^\pi$ is the coefficient of the energy of the level $\varepsilon_{\ell\nu}^\pi = \alpha_\pi + \lambda_{\ell\nu}^\pi \beta_\pi$ and α_π and β_π are the standard Coulomb and the standard resonance integrals of π orbitals. And from the inclination of the line was estimated the value of the resonance integral β_π to be -2.23 eV, which seemed to be reasonable in comparison with the value estimated from other physicochemical sources. The higher the energy of the level lies, that is, the smaller the value of $\lambda_{\ell\nu}^\pi$ is, the less reducible the hydrocarbon is and, therefore, the more negative the half-wave reduction potential is.

Similar linear relationship between the lowest unoccupied π levels and reduction potentials and similar value of the integral $\beta\pi$ have been found for a variety of compounds such as substituted stilbenes, substituted nitrobenzenes, aromatic ketones and vinyl compounds.³⁾

Furthermore, the structures of products of corresponding controlled potential electrolysis of hydrocarbons were discussed in terms of the π electron distribution of the hydrocarbon anions,²⁾ in which an excess electron is accepted in the lowest unoccupied π levels and from which products will be yielded by protonation. Protons add to those positions which have a large electron density and a product results in which a double bond or more are reduced. For instance naphthalene is reduced to give 1,2-dihydronaphthalene and 1,4-dihydronaphthalene.

On the other hand, it has been elucidated that halogenated saturated hydrocarbons are polarographically reducible, showing half-wave potentials independent of pH and giving products in which carbon-halogen bonds are reduced to carbon-hydrogen bonds.⁴⁾ For instance, the half-wave reduction potential of methyl iodide is -1.63 V vs. S.C.E. (saturated calomel electrode) and it is converted into methane when reduction is performed at that voltage. Further it would be

interesting to notice that some of the halogenated unsaturated hydrocarbons are reduced at the potential less negative than the potential at which the mother hydrocarbons are reducible, and carbon-halogen bonds are reduced in these compounds as well as in saturated halides.⁴⁾

With respect to the problems of polarographic reduction of saturated compounds which have no π conjugated system, theoretical studies have never been carried out in relation to their electronic structure.

The present authors have established a simple molecular orbital method for calculating the σ electronic structure of saturated hydrocarbons and their derivatives^{5,6)} and have applied the method further to discussing the electronic structure of σ skeleton in conjugated compounds.^{7,8)} By the aid of the method one can calculate energy levels and charge distribution of σ electrons.

In the present chapter, as to saturated halides at first, will be discussed relations between their half-wave reduction potentials and their lowest unoccupied σ levels and the connection of distribution of the lowest unoccupied level to structures of reduction products, and then, as for unsaturated halides, will be made similar discussions, and, at the end, a possibility that in polyhalogenated compounds

the lowest unoccupied σ level may creep below the lowest unoccupied π level will be suggested.

§2. Method of Calculation

Electronic structures of π and σ electron systems are calculated by using simple LCAO MO (linear-combination-of-atomic-orbital molecular orbital) method with overlap integrals and electronic interactions neglected.

In saturated compounds in which carbon atoms are sp^3 -hybridized, molecular orbitals are written as linear combinations of all σ atomic orbitals—hydrogen $1s$ orbitals, sp^3 -hybridized orbitals of carbons and σ atomic orbitals of halogens. The energy ε_i of the i th molecular orbital is expressed

$$\varepsilon_i = \alpha_{sp^3} + \lambda_i^{sp^3} \beta_{sp^3-sp^3} \quad (2)$$

where α_{sp^3} and $\beta_{sp^3-sp^3}$ mean the Coulomb integral of a sp^3 -hybridized orbital of carbon and the resonance integral between sp^3 orbitals making a standard σ bond. The larger value of $\lambda_i^{sp^3}$ corresponds to the lower energy since the resonance integral is minus in sign. The Coulomb and the resonance integrals of each atom and bond adopted in the calculation are the same as was employed previously,^{5,6)} which

would not be repeated for brevity.

The method can be extended to the calculation of electronic structures of conjugated compounds if, in this case, one regards the π electrons as making a field where σ electrons move. Then the energy of the i th σ molecular orbital, ε_i^σ , may be written as

$$\varepsilon_i^\sigma = \alpha_{sp^2} + \lambda_i^{sp^2} \beta_{sp^2-sp^2} \quad (3)$$

where α_{sp^2} and $\beta_{sp^2-sp^2}$ are the standard Coulomb and the standard resonance integrals of $sp^2 \sigma$ orbitals. And similarly the energy of the j th π molecular orbital calculated by the simple LCAO MO method is given as

$$\varepsilon_j^\pi = \alpha_\pi + \lambda_j^\pi \beta_\pi \quad (4)$$

Calculating σ electron densities could clearly explain experimental results of physicochemical properties----for instance, dipole moments, halogen coupling constants in PQR spectra, proton chemical shifts in NMR spectra----as was reported previously.^{7,8)}

A notable result of the calculation in halogenated compounds is that substitution of hydrogens by halogens does not change the energy of σ occupied levels so seriously but gives rise to a remarkable change of the energy of σ

unoccupied levels. Especially a considerable lowering of the lowest unoccupied σ level occurs and the lowering becomes larger as the number of halogen atoms increases.

§3. Polarographic Reduction and σ Electronic Structures of Haloalkanes

Haloalkanes belong to one of the few groups of compounds which include no conjugated system and can nevertheless be reduced polarographically. As was pointed out in the previous section, halogen substitution causes a lowering of the lowest unoccupied σ levels.

Imitating Eq. 1, we compared the first half-wave reduction potential of halomethanes with the energy of their lowest unoccupied σ level, expecting the following relation:

$$-E_{1/2} = \lambda_{ev} {}^s p^3 \beta_{sp^3-sp^3} + C' \quad (5)$$

As can be seen in Table I, a parallelism between them was obtained for each series of halomethanes. A similar relation is obtained also in haloethanes. Discrepancy which is observed in comparing bromo- and iodomethanes will be probably due to an inappropriate choice of energy parameters for halogen atomic orbitals which have never strictly tested nor improved, and also due to the effect of neglecting

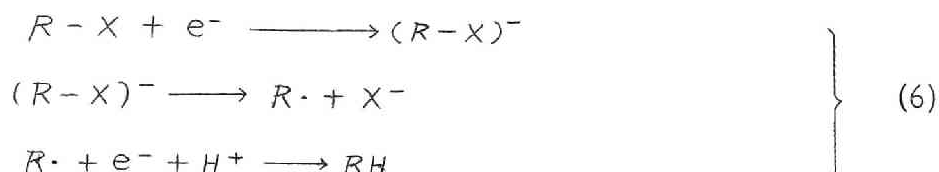
overlap integrals.

Although the linear relation represented by Eq. 5 was not precisely adopted to the values in Table I, we roughly estimated the magnitude of $\beta_{sp^3-sp^3}$ by means of Eq. 3 and were led to a value of ca. -5 eV. This value is very close to that of $\beta_{sp^3-sp^3}$ obtained in the discussion on NMR chemical shifts of halides (-5.7 eV)¹¹⁾ and also on ionization potentials of halides (ca. -5eV).¹¹⁾ And, furthermore, this would be rather rational in comparison with the above cited value of β_π , -2.23 eV.

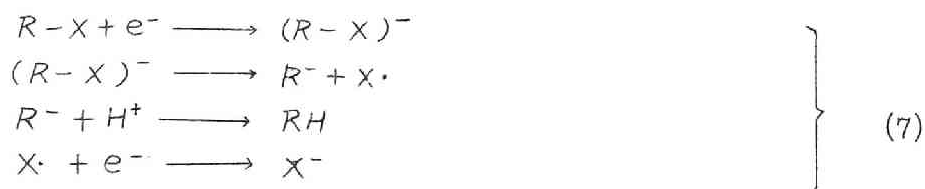
From these correspondences between $E_{1/2}$ and $\lambda_{lv}^{sp^3}$, it would safely be said that the potential-determining step in the polarographic reduction of haloalkanes would be the electron transfer from the electrode to their lowest unoccupied σ level. And the fact that methane and other saturated hydrocarbons do not give a reduction wave would be clear because of the high energy of its lowest unoccupied σ level.

The electron distribution of the lowest unoccupied level much localizes on the carbon-halogen bonds and the bond order of the level on the bond is negative and large in absolute value, as is seen in the fourth and fifth columns in Table I and Fig. 1. These calculated results suggest

that in a state which has an electron in that level the carbon-halogen bonds are very easy to break down. The anion, which might be produced at the first step of the polarographic reduction of halides, corresponds to this case. One may consider a second process in which a carbon-halogen bond of the anion breaks and the resultant anion, or radical, reacts with a proton, or with a proton and an electron, in the solution (75% dioxane-25% water was used as the solvent), as was suggested by Stackelberg and Stracke, to wit,



or



Thus, one may clearly explain theoretically the result of controlled potential reduction that, for instance, methyl bromide was reduced to give methane and ethyl bromide gave ethane. This connection seems to support the conclusion derived above that the first reduction potential of saturated

halides corresponds to the electron transfer to the lowest unoccupied σ level. It has not yet been decided in which one of the two mechanisms, Eqs. 6 and 7, the real break down of carbon-halogen bonds does occur. On the basis of the electron affinities of halogen and carbon atoms, the first mechanism, Eq. 6, seems to be more probable than the second one. If it is true, one who carries out the controlled potential electrolysis of halides in an aprotic solvent would be able to observe the ESR spectra of the radical.

§4. Polarographic Reduction and σ and π Electronic Structures of Conjugated Halides

In this section relations between the half-wave reduction potential and the energy of the lowest σ and the lowest π unoccupied levels are investigated. Experimental $E_{1/2}$ and calculated height of the lowest unoccupied levels, $\lambda_{lv}^{sp^2}$ and λ_{lv}^{π} , of chlorobenzenes and chloroethylenes, as an example, are tabulated in Table II.

The height of the lowest unoccupied π level hardly varies in these series and seems to have no concern with their half-wave reduction potential $E_{1/2}$. Even if one applies, by force, Eq. 1 to their relation, one would be led to an irrational result that the absolute value of β must

exceed 20 eV. On the other hand the height of the lowest unoccupied σ levels of these compounds is shown to be parallel to the half-wave potential, as well as in haloalkanes:

$$-E_{1/2} = \lambda_{lv}^{sp^2} \beta_{sp^2-sp^2} + C'' \quad (8)$$

and from the parallelism the magnitude of $\beta_{sp^2-sp^2}$ is estimated to be -6.88 eV (in the case of chlorobenzenes), a value which seems to be appropriate in view of those of β_π and $\beta_{sp^2-sp^2}$.

Furthermore, as to the reduction products, for instance, naphthalene from α -bromonaphthalene and ethylene from 1,2-diiodoethylene, an explanation similar to the case of haloalkanes would be possible based on the localizing and antibonding nature on the carbon-halogen bonds of the lowest unoccupied σ level, as is shown in Table II and Fig. 2.

Thus the polarographic reduction of conjugated halides would represent the electron transfer process from the cathode to the lowest unoccupied σ , not π , level, in contrast with the case of other conjugated compounds in which an electron runs into the lowest unoccupied π level, satisfying Eq. 1.

§5. Possible Inversion of Height of Energy

Levels and $\pi \rightarrow \sigma^*$ Transition

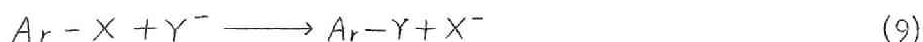
As the entropy change will not be very different between the both processes, the one in which the electron transfers to the σ unoccupied level and the one to the π unoccupied level, it may be said that the lowest unoccupied σ level would be lower than the lowest unoccupied π level. This conclusion would be more certain as the number of halogen atoms in the molecule increases or as the halogen changes in the order $F \rightarrow Cl \rightarrow Br \rightarrow I$.

One may raise an objection that the lowest unoccupied σ level into which an electron jumps may not be the lowest level of all, for, if the selective adsorption of carbon-halogen bonds might occur, an electron will have to run into the level localizing in the bonds. But the experimental result that α -bromonaphthalene is reduced at the voltage (-1.96 V) less negative than that at which naphthalene can first be reduced (-2.50 V) would reject the objection.

In Fig. 3 is shown the energy diagram of the lowest unoccupied levels which is mainly deduced from the linear relationship, Eqs. 1 and 8, between λ_{lv} and $E_{1/2}$. The value of energies of the levels might include errors of the

order 0.1 to 0.2eV. The origin of the energy is arbitrary. One can see the inversion of the π and σ lowest unoccupied levels.

There is a well-known fact that nucleophilic substitution of unsaturated halides exclusively takes place at the halogen atom, as follows:



where Y^- is a nucleophilic reagent. It seems very interesting to connect the fact with the inversion of energy levels. That is to say, for instance, when the reagent comes near the substrate, electrons on the substrate easily delocalize to the lowest unoccupied level, that is, the lowest unoccupied σ level, which causes a weakening of carbon-halogen bonds, and the substitution occurs. Therefore, the mechanism of nucleophilic substitution of unsaturated halides might differ from that of ordinary substitution reactions of conjugated compounds in which π levels play a dominant role.

And furthermore the inversion of the lowest unoccupied levels in unsaturated halides would result in a weak and broad transition from the highest occupied π level (the highest occupied of all) to the lowest unoccupied σ level

(the lowest unoccupied of all), which would be seen in the range of larger wave-lengths; and it may be named $\pi \rightarrow \sigma^*$ transition. An $\pi \rightarrow \sigma^*$ transition was observed in saturated halides by Mulliken et al,⁹⁾ but the $\pi \rightarrow \sigma^*$ transition in conjugated halides has not yet observed nor suggested. A more precise calculation by LCAO ASMÖ CI method which confirms the conclusion will be published elsewhere.¹⁰⁾

§6. Discussion

It would be worth while to notice that haloalkanes and alkylperoxides are the only saturated compounds that can be polarographically reduced. Alkylperoxide gives an almost pH-independent wave at the much less negative potential; for instance, methyl hydroperoxide is reduced at -0.25V both in 0.01N HCl and 0.01N NaOH. The calculated lowest unoccupied σ level in alkylperoxides, as well as in haloalkanes, is located very low. For instance,¹¹⁾

$$\text{CH}_3\text{OOH} \quad \lambda_{\ell\nu}^{sp^3} = -0.0956^*$$

$$\text{C}_2\text{H}_5\text{OOH} \quad \lambda_{\ell\nu}^{sp^3} = -0.0940$$

$$(\text{CH}_3)_3\text{COOH} \quad \lambda_{\ell\nu}^{sp^3} = -0.0898$$

The lowering of the lowest unoccupied σ level in peroxides would have an intimate connection with their polarographic reduction, as one may expect from the discussion on saturated

* Parameters used in the calculation will be published elsewhere.¹¹⁾

halides.

And the distribution of the lowest unoccupied level is very localizing on the oxygen-oxygen bond and the partial bond order on the bond is negative and large in absolute value(Fig. 4) Thus after the electron transfer to the level the break down of the bond will follow.

Generally speaking, the lowering of the lowest unoccupied level is expected if a compound has one or more bonds whose resonance integrals are relatively small and at the same time one or both atoms constructing the bond are relatively electronegative. Peroxides and halides are typical examples of this kind.

Inversion of the lowest unoccupied σ and the lowest unoccupied π level may occur in the case where lowering of the lowest unoccupied σ level is large as stated above and the lowest unoccupied π level remains rather high. An electronegative atom in the compound necessarily causes lowering of all levels, but when the atom has a lone pair to conjugate with neighboring atoms the lowest unoccupied π level stays relatively high. Conjugated halides discussed in the paper and some conjugated peroxides seem to be the unique examples where the inversion might be expected.

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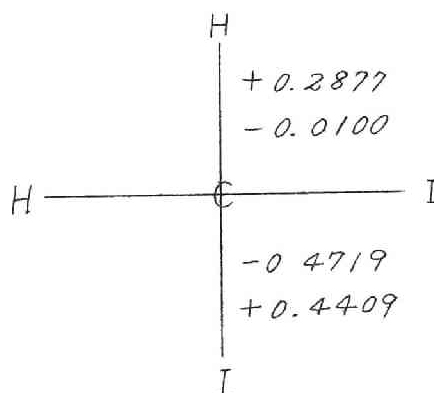


Fig. 1 Coefficients of atomic orbitals in the lowest unoccupied σ MO of diiodomethane

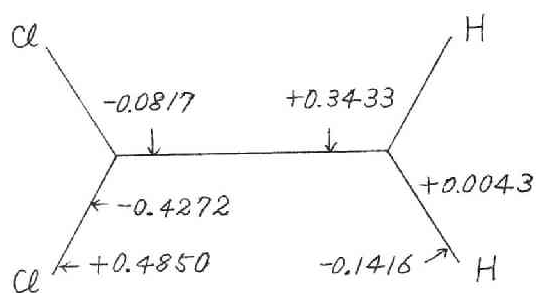


Fig. 2 Coefficients of atomic orbitals in the lowest unoccupied σ MO of 1,1-dichloroethylene

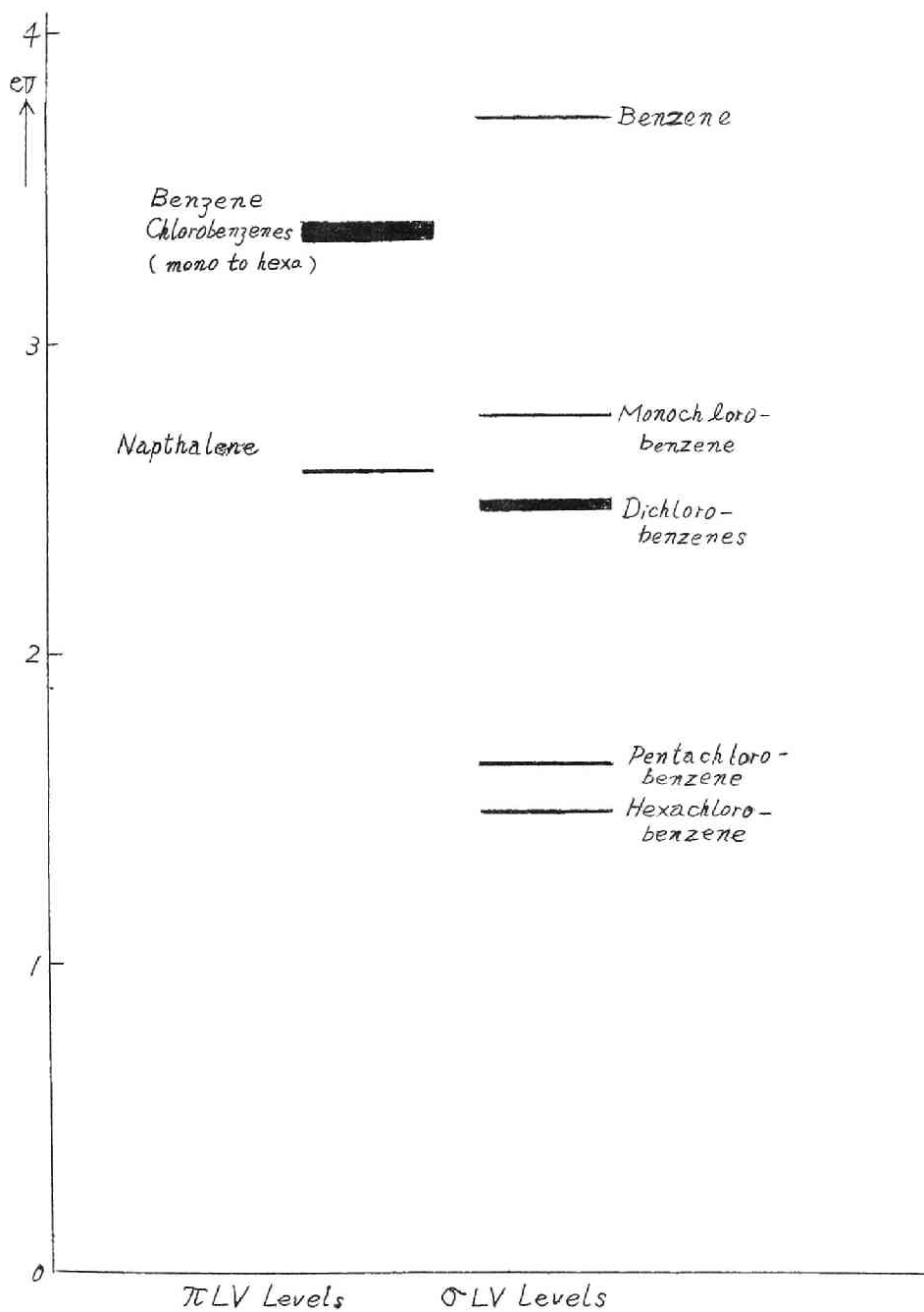


Fig. 3 Estimated lowest vacant π and σ Levels

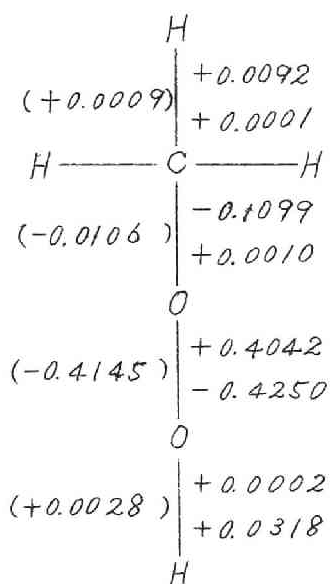


Fig. 4. Coefficient of atomic orbitals and partial bond order (in parentheses) of the lowest unoccupied molecular orbital of methyl hydroperoxide

Table I First Half-Wave Reduction Potential and Energy and Electron Distribution of the Lowest Unoccupied σ Level of Halomethanes

Compound	Half-Wave ⁴⁾ * Reduction Potential $E_{1/2}(V)$ vs.SCE	Energy of the Lowest Unoccupied Level $\lambda_{el}^{sp^3}$	Partial Bond Order of the Lowest Un- occupied Level on C-X Bond	Sum of the Distribution of the Lowest Unoccupied Level on C-X Bonds
CH ₄	NW	-0.848	---	0
CH ₃ Cl	-2.23	-0.400	-0.369	0.78
CH ₂ Cl ₂	-2.33	-0.229	-0.204	0.82
CHCl ₃	-1.67	-0.081	-0.147	0.89
CCl ₄	-0.78	+0.059	-0.116	1.00
CH ₃ Br	-1.63	-0.366	-0.375	0.79
CH ₂ Br ₂	-1.48	-0.190	-0.208	0.83
CHBr ₃	-0.64	-0.045	-0.144	0.87
CBr ₄	-0.3	+0.089	-0.112	1.00
CH ₃ I	-1.63	-0.337	-0.381	0.80
CH ₂ I ₂	-1.12	-0.167	-0.208	0.83
CHI ₃	-0.49	-0.027	-0.146	0.90
CI ₄	---	+0.095	-0.108	1.00

* NW indicates that the compound gives no reduction wave.

Table II. First Half-Wave Reduction Potential and Energy and Electron Distribution of the Lowest Unoccupied σ and the π Levels of Halogenobenzenes and Halogenoethylenes

1. Chlorobenzenes

Substituents	Half-Wave Reduction Potential ⁴⁾ $E_{1/2}$ (V)	Energy of the Lowest Unoccupied σ Level $\lambda_{\sigma}^{sp^2}$	Energy of the Lowest Unoccupied π Level $\lambda_{\pi}^{p^x}$	Partial Bond Order of the Lowest Unoccupied Level on C-X Bond	Sum of the Distribution of the Lowest Unoccupied Level on C-X Bonds
no	NW*	-0.501	-1.000	---	0
Cl	NW	-0.345	-0.983	-0.280	0.56
p-diCl	-2.49	-0.313	-0.967	-0.134	0.53
m-diCl	-2.48	-0.305	-0.991	-0.138	0.55
o-diCl	-2.51	-0.274	-0.973	-0.152	0.61
penta-Cl	---	-0.187	-0.967	-0.043	0.64
				-0.070	
				-0.079	
hexa-Cl	-1.44	-0.159	-0.951	-0.054	0.67

2. Chloroethylenes

no	NW	-0.664	-1.000	---	0
Cl	NW	-0.390	-0.975	-0.345	0.70
1,2-diCl	NW	-0.319	-0.951	-0.175	0.70
1,1-diCl	ca. -2.4	-0.229	-0.952	-0.207	0.84
tri-Cl	-2.14	-0.196	-0.928	-0.173	0.83
				-0.062	
tetra-Cl	-1.88	-0.129	-0.906	-0.105	0.89

*NW indicates that the compound gives no reduction wave.

Chapter 4
Electronic Spectra of Polyhalogenated
Conjugated Hydrocarbons

§1. Introduction

In Part II Chapter 2¹⁾ of this thesis the author has performed the simple LCAO MO calculation on σ electronic structures of conjugated halogenated hydrocarbons and found that substitution of hydrogen atoms in hydrocarbons by halogen atoms caused a remarkable lowering of the lowest unoccupied σ level. In the last chapter²⁾, from the discussion of the polarographic reduction of these compounds on the bases of the results in Chapter 2, a presumption that the lowest σ unoccupied level might be near or even lower than the lowest π unoccupied level. This inversion of the order of the energy levels was the most probable in polyhalogenated compounds.

In the experimental field absorption spectra of halogenated benzenes and ethylenes have been observed by many authors. In the former works such as by Lacher et al.³⁾ halogenated ethylenes---tetrachloroethylene, dichloroethylenes, vinyl chloride, dichlorodifluoroethylenes, trichlorofluoroethylene and so forth---showed a broad absorption which had no maximum

above 200 m μ . Also in halogenobenzenes no maximum has been observed and the shoulder in the longer wave length region have been attributed to the singlet $\pi \rightarrow$ triplet π^* transition.⁴⁾ Recent studies on tetraiodoethylene and tetrabromoethylene by Ito⁵⁾ have revealed two bands in the UV region and $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions have been suggested to be responsible to these bands.

Quantum chemical calculation of higher approximations (which means explicit inclusion of electronic interaction) on electronic structures of conjugated halogenated compounds has been carried out exclusively in the π electron approximation. Simonetta⁶⁾ calculated π MO's and π electronic energies of the ground and a few excited states of vinyl chloride (4 π electron system on 3 AO's) by semi-empirical LCAO SCF method.* Takekiyo⁷⁾ has made a valence bond calculation on π electronic energies of vinyl chloride.

In the present chapter the author is going to carry out an ASMO CI calculation on the transition energies of the lowest $\pi \rightarrow \sigma^*$ and the lowest $\pi \rightarrow \pi^*$ transitions of polyhalogenated compounds. The purpose of this chapter is to ascertain the presumption presented in Chapter 3, or in other

* His semi-empirical method of estimating nuclear penetration integrals seems to be too expedient to rely on.

words, to see which is the lowest transition of all. For this purpose the π electron approximation is of no use at all: σ electrons as well as π electrons has to be explicitly taken into account. One will understand the difficulty of this calculation caused by the increased number of electrons in question. For instance, vinyl chloride is a 4 electron system in the π electron approximation, but for the present purpose all the valence electrons, that is, 18 electrons (4π , 10σ and 4 lone pair electrons) have to be taken into calculation.

§2. Theoretical Method and Approximate

Evaluation of Atomic Integrals

One of the typical conjugated polyhalide would be tetrachloroethylene, which we shall employ for testing the possibility of $\pi \rightarrow \sigma^*$ transition. The compound is convenient because it is a polyhalide in which $\pi \rightarrow \sigma^*$ transition is more probable than in mono- or di-halide, and because it contains only two kinds of atoms, carbon and chlorine, which facilitates evaluating atomic integrals. Nevertheless, it consists of 36 valence electrons in 24 atomic orbitals. To carry out a precise and non-empirical calculation of electronic structures of this system is quite impossible for us who

cannot use the quickest computer. So we are obliged to make use of semi-empirical and approximate methods especially in estimating necessary atomic integrals. Approximations available for atomic integrals seem to be insufficient for our purpose to take explicitly σ electrons into account as well as π electrons, for there have been few examples of calculation on σ electronic structures of large molecules.

In the present section are described semi-empirical and approximate methods we use in evaluating atomic integrals and their results.

Atomic orbitals considered are 24 in all, i.e., 2s, 2p σ , 2p π and 2p π' orbitals on each carbon and 3s, 3p σ , 3p π and 3p π' orbitals on each chlorine. Two carbon and four chlorine atoms are named C₁, C₂, Cl₁, Cl₂, Cl₃ and Cl₄ as are shown in Fig. 1. The abbreviations as, ax, ay and az (a = 1,2) denote the name of the atomic orbitals or even the atomic wave functions themselves on the carbon C_a (a = 1,2) and similarly bS, bX, bY and bZ (b = 1, 2, 3, 4) those on the chlorine Cl_b (b = 1, 2, 3, 4). Coordinates for ax, ay, bX and bY are also given in Fig. 1 and az and bZ are directing upwards from the paper-plane. The geometry of the molecule is set as follows:⁸⁾ the C-C bond length 1.30Å and the C-Cl bond length 1.72Å and all the bond angles 120° with the planar

structure, and therefore, it belongs to the point group D_{2h} .

The overlap integrals are calculated theoretically by using Slater 2s, 2p, 3s and 3p orbitals, where the effective nuclear charges are taken to be 3.18 for carbon 2s and 2p orbitals and 6.099 for chlorine 3s and 3p orbitals. Representatives of the results are collected in Table I. Overlap integrals between non-neighboring atomic orbitals (they are in parentheses in Table I) are disregarded in all of the following estimations of integrals and calculations of electronic energies, for they seem to be small enough to affect little on the last result.

The Coulomb integrals which is defined by the equation

$$H_{rr} = \int \chi_r(1) H(1) \chi_r(1) d\tau, \quad (1)$$

is calculated by the so-called valence state energy approximation⁹⁾. $H(1)$ in Eq. 1 is the one-electron hamiltonian consisting of the kinetic energy $T(1)$ and the potential energies $U_\alpha(1)$ by the +4-charged carbon and the +7-charged chlorine cores, α :

$$H(1) = T(1) + \sum_{\alpha=1}^6 U_\alpha(1) \quad (2)$$

Extending the usual method in π electronic systems, H_{rr} may

be written as follows:

$$H_{rr} = W_r - \sum_{s \substack{(\neq r) \\ \text{(on the} \\ \text{core } \xi)}} (rr|ss) - \sum_{\alpha \substack{(\neq \xi)}} (\alpha:rr) \quad (3)$$

In deriving Eq. 3, W_r , the valence state energy of an electron on the r th AO, which is correlated to the valence state ionization potential, I_r , by

$$W_r = -I_r \quad (4)$$

is assumed to be the eigenvalue of the equation:

$$(\tau(1) + U_r^{+1}(1)) \chi_r = W_r \chi_r \quad (5)$$

where U_r^{+1} is the potential energy of the electron 1 on the cores ξ caused by the +1-charged core ξ . And necessary values of I_r and the valence state electron affinity, E_r , are evaluated by Moffit's method¹⁰⁾ and Moore's Table 1¹¹⁾ except for those available in Pritchard and Skinner's paper¹²⁾.

The values are given in Table II. In the present chapter all the energies are written in units of eV. $(rr|ss)$ and $(\alpha:rr)$ in Eq. 3 are the Coulomb repulsion integral and the Coulomb penetration integral, respectively, of each of which the definition and the method of evaluation will be given

later. $\sum_{s \substack{(\neq r) \\ \text{(on the} \\ \text{core } \xi)}}$ should cover 35 electrons and $\sum_{\alpha \substack{(\neq \xi)}}$ 5 cores.

Calculated values of H_{rr} are given in Table III.

One-electron resonance integral is derived to be given by the following equation, if one applies here also the valence state energy approximation:

$$H_{rs} = (S_{rs}/4) [2H_{rr} + 2H_{ss} + 2(rr|ss) - (rr|rr) - (ss|ss) - (\alpha_r:rr) - (\alpha_s:ss) + (\alpha_r:ss) + (\alpha_s:rr)] \quad (5)$$

where α_r denotes the core on which the orbital r stands. The values of the one-electron resonance integral thus calculated are collected in Table IV.

Electron repulsion integrals $(rt|su)$, defined by

$$(rt|su) = \int \chi_r(1) \chi_t(1) (e^2/r_{12}) \chi_s(2) \chi_u(2) d\tau_1 d\tau_2 \quad (6)$$

are classified into several classes. As their semi-empirical bases, the one-center one-orbital integral $(rr|rr)$ is fitted to the experimental value in Table I by the equation:

$$(rr|rr) = I_r - E_r \quad (7)$$

Effective nuclear charges, which are to be used in evaluating other one-center and all two-center repulsion integrals, are decided so that these semi-empirical values may fit the theoretical results of the integral (with Slater orbitals). In order to simplify the numerical calculation, the valence orbitals on chlorine are expressed by 2s and 2p orbitals

instead of actual 3s and 3p orbitals, and the effective nuclear charges are decided for these orbitals. The values are : $Z_{c2s} = 2.463$, $Z_{c2p} = 2.036$, $Z_{c12s} = 2.171$ and $Z_{c12p} = 2.117$; and for integrals between the orbitals of different Z values the geometrical mean of them is employed. This approximation would not be serious, for the values of integrals by using 2s and 2p orbitals is ascertained in a few examples not to differ so much from those by 3s and 3p orbitals. The one center repulsion integrals of the type $(rr|ss)$ (r and s are on the same core) are calculated theoretically by using Slater 2s and 2p orbitals with the effective nuclear charges obtained now.

Two-center repulsion integrals of the type $(rr|ss)$ (r and s are not on the same core) also are calculated by the same method.

The values of the one-center and the two-center repulsion integrals of the types $(rr|rr)$ and $(rr|ss)$ obtained by this method are tabulated in Table V, in which the values with asterisk at the shoulder are what were gotten by Eq. 7.

Other kinds of the repulsion integrals $(rt|su)$, in which multi-center integrals are included, are approximated by the equation⁶⁾:

$$\begin{aligned}
 (rt|su) = (1/4) S_{rt} S_{su} [& (rr|ss) + (rr|uu) \\
 & + (tt|uu) + (tt|ss)]
 \end{aligned}
 \tag{8}$$

which is a little different from Mulliken's popular method¹³⁾ but is more convenient for numerical calculation than it.

One-center nuclear penetration integrals ($\alpha_r:rr$) are calculated theoretically by the formulas derived anew following Parr's method¹³⁾; in this calculation are used for carbon 2s and 2p orbitals with $Z = 3.18$ and for chlorine 3s and 3p orbitals with $Z = 6.099$. The values with asterisk on the shoulder in Table VI are obtained in this manner. Two-center penetration integrals of the type ($\alpha_s:rr$), which are in general small in magnitude, may be roughly approximated. In the present chapter, no matter what are the atoms to which α_s and r belong, the two-center penetration integral is approximated by the theoretical values of the integral between the carbon neutral atom and the carbon orbital with $Z = 3.18$ at the actual distance, except for the integral in which α_s is chlorine neutral atom, where the integral for carbon nucleus is multiplied by a theoretically derived factor 7/4. Newly derived formulas of the two-center penetration integral between a carbon atom and 2s, 2p orbitals, are given in Table VII. The calculated values of the two-center penetration integrals

are collected in Table VI.

Since the compound has the D_{2h} symmetry, symmetry orbitals (SO's) would be more convenient than AO's themselves. In Table VIII unnormalized symmetry orbitals are tabulated.

Molecular orbitals which are used as bases of ASMO CI calculation are decided by the simple LCAO MO calculation separately for π and σ electrons, with the same energy parameters as in the previous papers^{1,2)} and with including neighboring overlap integrals. The MO's thus obtained are collected in Table IX. Numbering of the MO's in each group of σ MO's (abbreviation σ) and π MO's (π) begins from the MO of the lowest energy up to those of higher energy.

The symmetry orbitals Y_1 , Y_2 , Y_3 and Y_4 and S_1 , S_2 , S_3 and S_4 are assumed not to enter into conjugation with other orbitals of the same symmetry and to make lone pairs by themselves. Abbreviations n and ℓ are given to the 3p and 3s lone pairs of chlorine atoms, respectively.

36 Electrons in the molecule occupy the following 18 MO's: ℓ_1 to ℓ_4 , n_1 to n_4 , σ_1 to σ_5 and π_1 to π_5 .

§3. The Lowest $\pi \rightarrow \pi^*$ and the Lowest $\pi \rightarrow \sigma^*$

Transitions in Tetrachloroethylene

In the present section an ASMO CI calculation of tran-

sition energy in tetrachloroethylene is to be presented.

At first the one-electron transitions are classified according to the symmetry of the molecule in Table X, where $a \rightarrow b$ means the state in which the one-electron transition from the occupied MO a to the unoccupied MO b occurred. In the table are also shown which irreversible representation components of electric moments belong to.

The configurations of the lowest energy, in which we are interested, would be $\pi 5 \rightarrow \pi 6$ configuration of all $\pi \rightarrow \pi^*$ transitions and $\pi 5 \rightarrow \sigma 6$ of all $\pi \rightarrow \sigma^*$ transitions. Since the MO's are not good enough to calculate actual transition energies by a single configuration, a configuration interaction calculation seems to be indispensable.

Configuration interaction of $\pi 5 \rightarrow \pi 6$ with $\pi 1 \rightarrow \pi 6$ is carried out to get a better approximation of the lowest $\pi \rightarrow \pi^*$ transition; interaction of the configuration $\pi 5 \rightarrow \pi 6$ with other configurations than $\pi 1 \rightarrow \pi 6$ of the same symmetry would affect the result little. $\pi 5 \rightarrow \sigma 6$ transition is considered without any configuration interaction as the upper limit of the lowest $\pi \rightarrow \sigma^*$ transition.

Possibility of the so-called $n \rightarrow \pi^*$ transition appearing in lower frequency region would be small, for the energies of the 3s and 3p lone pairs of chlorine atom seem relatively

low because of its large electronegativity.

As we can see in Table X, in tetrachloroethylene the lowest singlet $\pi \rightarrow \pi^*$ (${}^1B_{3u}$) transition is allowed, whose transition moment is parallel to the C-C axis. The lowest singlet $\pi \rightarrow \sigma^*$ (${}^1B_{2g}$) transition in which we are most interested, however, is forbidden by symmetry. In this section, therefore, we are only going to make a theoretical comparison of energies of the $\pi \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions. On the transition moment a brief discussion is to be given in the next section.

Interconfigurational matrix element $\langle \pi 5 \rightarrow \pi 6 | \mathcal{H} | \pi 1 \rightarrow \pi 6 \rangle$ between the $\pi 5 \rightarrow \pi 6$ configuration and the $\pi 1 \rightarrow \pi 6$ configuration is given by the following formula:

$$\begin{aligned} {}^{1,3} \langle \pi 5 \rightarrow \pi 6 | \mathcal{H} | \pi 1 \rightarrow \pi 6 \rangle &= (1 \pm 1) \langle \pi 1 \pi 6 | \pi 5 \pi 6 \rangle \\ &- \langle \pi 1 | \mathcal{H} | \pi 5 \rangle - \sum_j' \langle \pi 1 \pi 5 | jj \rangle + \sum_k'' \langle \pi 1 k | \pi 5 k \rangle \end{aligned} \quad (9)$$

where the matrix element between the singlet states corresponds to the upper sign and that between triplet to the lower. \mathcal{H} is the total hamiltonian of the system, $(ab|cd)$ is the electronic repulsion integral among MO's a, b, c and d and is defined:

$$\langle ab|cd \rangle = \int a(1)b(1) (\pm^2/r_{12}) c(2)d(2) d\tau_1 d\tau_2 \quad (10)$$

and $\langle a | H | b \rangle$ is the one-electron integral between MO's a and b , defined:

$$\langle a | H | b \rangle = \int a(1) H(1) b(1) d\tau_1 \quad (11)$$

$H(1)$ being the one-electron hamiltonian defined by Eq. 2.

\sum_j' means the twice sum over all occupied MO's in the ground state except $\pi 6$ and $\pi 1$, and the sum over $\pi 6$, $\pi 1$ and $\pi 5$. \sum_k'' is the sum over $\pi 2$, $\pi 3$, $\pi 4$ and $\pi 6$.

Energies of the configurations and the interconfigurational matrix elements and CI eigenvalues are collected in Table XI.

The last result of the calculated energies of the lowest $\pi \rightarrow \pi^*$ (singlet and triplet) and the lowest $\pi \rightarrow \sigma^*$ (singlet) transitions are shown in Table XII.[†] In the table we can clearly see that the singlet $\pi \rightarrow \sigma^*$ transition energy is calculated to be remarkably smaller than that of the lowest $\pi \rightarrow \pi^*$ transition. Though the result will depend on the approximation, this may be a theoretical support on the authors' presumption that the lowest σ unoccupied level might be lower than the lowest π unoccupied level in conjugated halogenated hydrocarbons, most possibly in polyhalides.

[†]Triplet $\pi \rightarrow \sigma^*$ is not considered at all, for it will be too weak to be observed.

§4. Discussion

As we have seen in the preceding section, the lowest $\pi \rightarrow \sigma^*$ transition in tetrachloroethylene is forbidden by symmetry. Transition moment of the $\pi \rightarrow \sigma^*$ transition will be in general, except for the case forbidden by symmetry, of the order or a little less than that of $n \rightarrow \sigma^*$ transitions, for the orbital π is a kind of localized π orbital.

Transition moments for the lowest $\pi \rightarrow \sigma^*$ transition as well as for the lowest $\pi \rightarrow \pi^*$ transition are calculated in less symmetric halides such as trichloroethylene and 1,2-dichloroethylene. Necessary MO's are decided by the simple LCAO method and the atomic integrals of the type $(s|\chi|t)$, defined by Eq. 12, are calculated theoretically by the use

of Slater 2s, 2p and 3p orbitals with the effective nuclear charges $Z_{C,2s} = Z_{C,2p} = 3.18$ and $Z_{Cl,3p} = 6.099$

$$(s|\chi|t) = \int \chi_s(r) \chi_t(r) dr$$

Since in both compounds the lowest σ^* unoccupied orbital is strong localized in C-Cl bonds, the contribution of the moment integral between carbon atoms are neglected: the integrals taken into calculation are $(C13p\pi|z|C2p\sigma)$, $(C13p\pi|z|C2s)$ and $(C13p\sigma|z|C2p\pi)$, between the neighboring atoms. The values of the transition moments thus obtained are given in

Table XIII. Oscillator strengths cannot be calculated because of lack of our knowledge of transition energies in these compounds.

Comparison of the moments in Table XIII suggests that the $\pi \rightarrow \sigma^*$ transition is a little weaker than the $n \rightarrow \sigma^*$ transition as expected above, but it would not be too weak to be observed by a careful experiment and analysis.

There has been presented no experimental result that proves or suggests the possibility of the $\pi \rightarrow \sigma^*$ transition in the range of longer wave length. Most careful and precise measurements of the UV absorption spectra of conjugated polyhalides is anticipated very eagerly in this connection.

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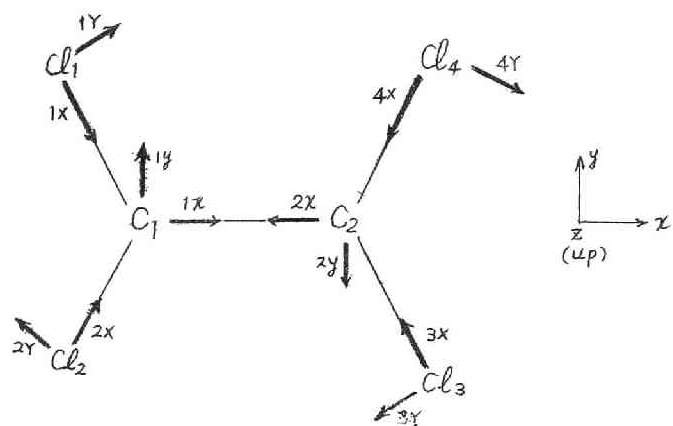


Fig. 1 Coordinates for atomic orbitals

Table I. Overlap Integrals between atomic orbitals Srs

AO r	AO s								
	s	1s	1x	1y	1z	1S	1X	1Y	1Z
1s	1	0	0	0	0	0.3100	0.3378	0	0
1x	0	1	0	0	0	-0.1960	-0.1892	0.1420	0
1y	0	0	1	0	0	0.2989	0.2885	0.1892	0
1z	0	0	0	1	1	0	0	0	0.1698
2s	0.5075	0.4706	0	0	0	(0.0703)	(0.0902)	0	0
2x	0.4706	0.2923	0	0	0	(0.0835)	(0.1009)	(0.0295)	0
2y	0	0	-0.3339	0	0	(-0.0535)	(-0.0519)	(-0.0475)	0
2z	0	0	0	0.3339	0	0	0	0	(0.0264)
1S	0.3100	-0.1960	0.2989	0	0	1	0	0	0
1X	0.3378	-0.1892	0.2885	0	0	0	1	0	0
1Y	0	0.1420	0.1892	0	0	0	0	1	0
1Z	0	0	0	0.1698	0	0	0	0	1

2S	0.3100	-0.1960	-0.2989	0	(0.0402)	(0.0478)	(-0.0313)	0
2X	0.3378	-0.1892	-0.2885	0	(0.0478)	(0.0608)	(-0.0314)	0
2Y	0	-0.1420	0.1892	0	(0.0313)	(0.0314)	(0.0154)	0
2Z	0	0	0	0.1698	0	0	0	(0.0129)
3S	(0.0703)	(0.0835)	(-0.0535)	0	(0.0014)	(0.0021)	(0.0006)	0
3X	(0.0902)	(0.1009)	(-0.0519)	0	(0.0021)	(0.0032)	(0.0014)	0
3Y	0	(0.0295)	(-0.0475)	0	(0.0006)	(0.0014)	(-0.0001)	0
3Z	0	0	0	(0.0264)	0	0	0	(0.0003)
4S	(0.0703)	(0.0835)	(0.0535)	0	(0.0207)	(0.0166)	(-0.0253)	0
4X	(0.0902)	(0.1009)	(0.0519)	0	(0.0166)	(0.0176)	(-0.0175)	0
4Y	0	(-0.0295)	(-0.0475)	0	(0.0253)	(-0.0175)	(0.0291)	0
4Z	0	0	0	(0.0264)	0	0	0	(0.0061)

Table II Valence State Ionization Potential and Electron Affinity

		Ionization Potential	Ir	Electron Affinity	Er
C	2s	21.43		9.26	
	2p	11.42		0.58	
Cl	3s	25.27		14.54	
	3p	15.09		3.82	

Table VI One-center and Two-center Penetration Integrals
(α : rY)

Core α	C ₁	C ₂	Cl ₁	Cl ₂	Cl ₃	Cl ₄
orbital r						
1s	23.660*	3.522	1.643	1.643	0.047	0.047
1x	23.660*	6.986	3.187	3.187	0.072	0.072
1y	23.660*	1.198	0.427	0.427	0.019	0.019
1z	23.660*	1.198	0.427	0.427	0.007	0.007
1S	0.939	0.027	29.124*	0.182	0	0
1X	1.821	0.041	29.124*	0.229	0	0
1Y	0.244	0.011	29.124*	0.112	0	0
1Z	0.244	0.004	29.124*	0.023	0	0

Table III One-electron Coulomb Integrals, H_{rr}

Orbital r	Integral
1s	-274,862
1x	-269,284
1y	-255,902
1z	-244,474
1S	-228,787
1X	-233,063
1Y	-214,864
1Z	-209,240

Table IV One-electron Resonance Integrals, H_{rs}

Orbitals			Orbitals		
r	s	Integral	r	s	Integral
1s	2s	-145.36	1s	1S	-82.552
1s	2x	-132.89	1s	1X	-90.493
1x	2x	-81.392	1x	1S	+51.521
1y	2y	+89.672	1x	1X	+50.087
1z	2z	-85.856	1x	1Y	-36.409
			1y	1S	-76.712
			1y	1X	-74.589
			1y	1Y	-47.350
			1z	1Z	-41.087

Table V One-Center and Two-Center Coulomb Repulsion Integrals of the Types $(rr|ss)$
and $(rr|rr)$

AO s AO r	1s	1x	1 ly	1z	1S	1X	1Y	1Z
1s	12.17*	11.066	11.066	11.066	7.602	8.206	7.149	7.149
1x	11.066	10.84*	9.672	9.672	7.457	7.830	7.070	6.866
1y	11.066	9.672	10.84*	9.672	7.888	8.207	7.353	7.266
1z	11.066	9.672	9.672	10.84*	7.149	7.561	6.580	6.868
2s	9.167	9.406	8.422	8.422	5.398	5.634	5.220	5.116
2x	9.406	9.169	8.467	8.467	5.557	5.892	5.414	5.273
2y	8.422	8.467	7.987	7.489	5.297	5.578	5.180	5.028
2z	8.422	8.467	7.489	7.987	5.116	5.346	4.955	4.932
1S	7.602	7.457	7.888	7.149	10.73*	10.560	10.560	10.560
1X	8.206	7.830	8.207	7.561	10.560	11.27*	9.953	9.953
1Y	7.149	7.070	7.353	6.580	10.560	9.953	11.27*	9.953
1Z	7.149	6.866	7.266	6.868	10.560	9.953	9.953	11.27*

2S	7.602	7.457	7.888	7.149	4.955	5.148	4.932	4.770
2X	8.206	7.830	8.207	7.561	5.148	5.378	5.132	4.927
2Y	7.149	7.070	7.353	6.580	4.932	5.132	4.923	4.730
2Z	7.149	6.866	7.266	6.868	4.770	4.927	4.730	4.633
3S	5.398	5.557	5.297	5.116	3.354	3.472	3.301	3.288
3X	5.634	5.892	5.578	5.346	3.472	3.621	3.410	3.394
3Y	5.220	5.414	5.180	4.955	3.301	3.410	3.254	3.234
3Z	5.116	5.273	5.028	4.932	3.288	3.394	3.234	3.231
4S	5.398	5.557	5.297	5.116	4.498	4.497	4.654	4.378
4X	5.634	5.892	5.578	5.346	4.497	4.474	4.641	4.322
4Y	5.220	5.414	5.180	4.955	4.654	4.641	5.964	4.487
4Z	5.116	5.273	5.028	4.932	4.378	4.322	4.487	4.237

Table VII Penetration Integral between Carbon Atom and 2S, 2p Orbitals

$$(C : ss) = \frac{Ze^{-\rho}}{40320} \left\{ 7\rho^6 + 49\rho^5 + 546\rho^4 + 4410\rho^3 + 12285\rho^2 + 23625(\rho + 1) \right\}$$

$$(C : \sigma\sigma) = \frac{Ze^{-\rho}}{40320} \left\{ 9\rho^6 + 123\rho^5 + 1236\rho^4 + 9618\rho^3 + 17493\rho^2 + 23625(\rho + 1) \right\}$$

$$(C : \pi\pi)^a = \frac{Ze^{-\rho}}{40320} \left\{ 12\rho^5 + 201\rho^4 + 1806\rho^3 + 9681\rho^2 + 23625(\rho + 1) \right\}$$

Z : effective nuclear charge

$\rho = ZR/a_0$ (a_0 : Bohr radius; R : interatomic distance)

S, σ , π : 2S, 2p σ , 2p π orbital

a) Ref. 13.

Table VIII Symmetry Orbitals of Tetrachloroethylene

Symmetry	Carbon	Chlorine
a_g	$s_1 = 1s + 2s$	$S_1 = 1S + 2S + 3S + 4S$
	$x_1 = 1x + 2x$	$X_1 = 1X + 2X + 3X + 4X$
		$Y_1 = 1Y - 2Y + 3Y - 4Y$
b_{3u}	$s_2 = 1s - 2s$	$S_2 = 1S + 2S - 3S - 4S$
	$x_2 = 1x - 2x$	$X_2 = 1X + 2X - 3X - 4X$
		$Y_2 = 1Y - 2Y - 3Y + 4Y$
b_{1g}	$y_3 = 1y + 2y$	$S_3 = 1S - 2S + 3S - 4S$
		$X_3 = 1X - 2X + 3X - 4X$
		$Y_3 = 1Y + 2Y + 3Y + 4Y$
b_{2u}	$y_4 = 1y - 2y$	$S_4 = 1S - 2S - 3S + 4S$
		$X_4 = 1X - 2X - 3X + 4X$
		$Y_4 = 1Y + 2Y - 3Y - 4Y$
b_{1u}	$z_5 = 1z + 2z$	$Z_5 = 1Z + 2Z + 3Z + 4Z$
b_{2g}	$z_6 = 1z - 2z$	$Z_6 = 1Z + 2Z - 3Z - 4Z$
a_u		$Z_7 = 1Z - 2Z + 3Z - 4Z$
b_{3g}		$Z_8 = 1Z - 2Z - 3Z + 4Z$

Table IX MO's of Tetrachloroethylene

$$\begin{aligned}
 \pi 1 (b_{1u}) &= 0.4401 Z_5 + 0.1994 Z_5 \\
 \pi 2 (b_{2g}) &= 0.4704 Z_6 + 0.1392 Z_6 \\
 \pi 3 (a_u) &= 0.5000 Z_7 \\
 \pi 4 (b_{3g}) &= 0.5000 Z_8 \\
 \pi 5 (b_{1u}) &= -0.2601 Z_5 + 0.5933 Z_5 \\
 \pi 6 (b_{2g}) &= -0.2289 Z_6 + 0.8958 Z_6 \\
 \sigma 1 (b_{3u}) &= 0.0607 X_2 - 0.0911 x_2 + 0.8341 s_2 \\
 \sigma 2 (a_g) &= 0.1161 X_1 - 0.0479 x_1 + 0.5200 s_1 \\
 \sigma 3 (b_{1g}) &= 0.3906 X_3 + 0.2996 y_3 \\
 \sigma 4 (b_{2u}) &= 0.4009 X_4 + 0.2314 y_4 \\
 \sigma 5 (a_g) &= 0.2884 X_1 - 0.4088 x_1 - 0.1390 s_1 \\
 \sigma 6 (b_{3u}) &= 0.6276 X_2 + 0.1970 x_2 - 0.7215 s_2 \\
 \sigma 7 (a_g) &= 0.5119 X_1 + 0.6017 x_1 - 0.4662 s_1 \\
 \sigma 8 (b_{2u}) &= 0.3534 X_4 - 0.6122 y_4 \\
 \sigma 9 (b_{1g}) &= 0.4251 X_3 - 0.9545 y_3 \\
 \sigma 10 (b_{3u}) &= 0.4797 X_2 - 1.6011 x_2 - 2.2511 s_2 \\
 l 1 (a_g) &= 0.5000 S_1 \\
 l 2 (b_{3u}) &= 0.5000 S_2 \\
 l 3 (b_{1g}) &= 0.5000 S_3 \\
 l 4 (b_{2u}) &= 0.5000 S_4 \\
 n 1 (a_g) &= 0.5000 Y_1 \\
 n 2 (b_{3u}) &= 0.5000 Y_2 \\
 n 3 (b_{1g}) &= 0.5000 Y_3 \\
 n 4 (b_{2u}) &= 0.5000 Y_4
 \end{aligned}$$

Table XI Configurational Matrix Elements of B_{3u} Transitions

$$^3\langle \pi 5 \rightarrow \pi 6 | \mathcal{H} | \pi 5 \rightarrow \pi 6 \rangle = E_0 + 10.730$$

$$^3\langle \pi 1 \rightarrow \pi 6 | \mathcal{H} | \pi 1 \rightarrow \pi 6 \rangle = E_0 + 14.221$$

$$^3\langle \pi 5 \rightarrow \pi 6 | \mathcal{H} | \pi 1 \rightarrow \pi 6 \rangle = 2.044$$

$$^3\varepsilon_+ = E_0 + 9.788$$

$$^3\varepsilon_+ = E_0 + 15.163$$

$$^1\langle \pi 5 \rightarrow \pi 6 | \mathcal{H} | \pi 5 \rightarrow \pi 6 \rangle = E_0 + 13.702$$

$$^1\langle \pi 1 \rightarrow \pi 6 | \mathcal{H} | \pi 1 \rightarrow \pi 6 \rangle = E_0 + 14.719$$

$$^1\langle \pi 5 \rightarrow \pi 6 | \mathcal{H} | \pi 1 \rightarrow \pi 6 \rangle = 2.770$$

$$^1\varepsilon_+ = E_0 + 11.394$$

$$^1\varepsilon_+ = E_0 + 17.025$$

E_0 : the energy of the ground state

Table XII Calculated Lowest Transition Energies of
Tetrachloroethylene

Transition	Symmetry	Transition Energy	Strength
$\pi \rightarrow \pi^*$	$^3B_{3u}$	9.8	forbidden
	$^1B_{3u}$	11.4	allowed
$\pi \rightarrow \sigma^*$	$^1B_{2g}$	6.9	forbidden

Table X Classification of one-electron

	A_g	A_u	B_{1g}	B_{1u}
$\pi \rightarrow \pi^*$	$\pi_2 \rightarrow \pi_6$		$\pi_4 \rightarrow \pi_6$	
$\pi \rightarrow \sigma^*$		$\pi_4 \rightarrow \sigma_6$ $\pi_3 \rightarrow \sigma_7$ $\pi_5 \rightarrow \sigma_9$ $\pi_2 \rightarrow \sigma_8$ $\pi_4 \rightarrow \sigma_{10}$ $\pi_1 \rightarrow \sigma_9$		$\pi_5 \rightarrow \sigma_7$ $\pi_4 \rightarrow \sigma_8$ $\pi_3 \rightarrow \sigma_9$ $\pi_2 \rightarrow \sigma_6$ $\pi_2 \rightarrow \sigma_{10}$ $\pi_1 \rightarrow \sigma_7$
$n \rightarrow \pi^*$		$n_4 \rightarrow \pi_6$		$n_2 \rightarrow \pi_6$
$n \rightarrow \sigma^*$	$n_2 \rightarrow \sigma_6$ $n_1 \rightarrow \sigma_7$ $n_4 \rightarrow \sigma_8$ $n_3 \rightarrow \sigma_9$ $n_2 \rightarrow \sigma_{10}$		$n_4 \rightarrow \sigma_6$ $n_3 \rightarrow \sigma_7$ $n_2 \rightarrow \sigma_8$ $n_1 \rightarrow \sigma_9$ $n_4 \rightarrow \sigma_{10}$	
$\sigma \rightarrow \pi^*$		$\sigma_4 \rightarrow \pi_6$		$\sigma_1 \rightarrow \pi_6$
$\sigma \rightarrow \sigma^*$	$\sigma_5 \rightarrow \sigma_7$ $\sigma_4 \rightarrow \sigma_8$ $\sigma_2 \rightarrow \sigma_7$ $\sigma_3 \rightarrow \sigma_9$ $\sigma_1 \rightarrow \sigma_6$ $\sigma_1 \rightarrow \sigma_{10}$		$\sigma_4 \rightarrow \sigma_6$ $\sigma_3 \rightarrow \sigma_7$ $\sigma_5 \rightarrow \sigma_9$ $\sigma_4 \rightarrow \sigma_{10}$ $\sigma_2 \rightarrow \sigma_9$ $\sigma_1 \rightarrow \sigma_8$	
moment	forbidden	forbidden	forbidden	z

Transitions of Tetrachloroethylene

B_{2g}	B_{2u}	B_{3g}	B_{3u}
	$\pi_3 \rightarrow \pi_6$		$\pi_5 \rightarrow \pi_6$ $\pi_1 \rightarrow \pi_6$
$\pi_5 \rightarrow \sigma_6$ $\pi_3 \rightarrow \sigma_8$ $\pi_2 \rightarrow \sigma_7$ $\pi_4 \rightarrow \sigma_9$ $\pi_5 \rightarrow \sigma_{10}$ $\pi_1 \rightarrow \sigma_6$ $\pi_1 \rightarrow \sigma_{10}$		$\pi_5 \rightarrow \sigma_8$ $\pi_4 \rightarrow \sigma_7$ $\pi_3 \rightarrow \sigma_6$ $\pi_3 \rightarrow \sigma_{10}$ $\pi_2 \rightarrow \sigma_9$ $\pi_1 \rightarrow \sigma_8$	
$\pi_1 \rightarrow \pi_6$		$\pi_3 \rightarrow \pi_6$	
	$\pi_3 \rightarrow \sigma_6$ $\pi_4 \rightarrow \sigma_7$ $\pi_1 \rightarrow \sigma_8$ $\pi_2 \rightarrow \sigma_9$ $\pi_3 \rightarrow \sigma_{10}$		$\pi_1 \rightarrow \sigma_6$ $\pi_2 \rightarrow \sigma_7$ $\pi_3 \rightarrow \sigma_8$ $\pi_4 \rightarrow \sigma_9$ $\pi_1 \rightarrow \sigma_{10}$
$\sigma_5 \rightarrow \pi_6$ $\sigma_2 \rightarrow \pi_6$		$\sigma_3 \rightarrow \pi_6$	
	$\sigma_5 \rightarrow \sigma_8$ $\sigma_4 \rightarrow \sigma_7$ $\sigma_3 \rightarrow \sigma_6$ $\sigma_2 \rightarrow \sigma_8$ $\sigma_3 \rightarrow \sigma_{10}$ $\sigma_1 \rightarrow \sigma_9$		$\sigma_5 \rightarrow \sigma_6$ $\sigma_3 \rightarrow \sigma_8$ $\sigma_2 \rightarrow \sigma_6$ $\sigma_4 \rightarrow \sigma_9$ $\sigma_5 \rightarrow \sigma_{10}$ $\sigma_1 \rightarrow \sigma_7$ $\sigma_2 \rightarrow \sigma_{10}$
forbidden	y.	forbidden	x

Table XIII Approximate Values of Transition Moments of
 $\pi \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ Transitions of Some
 Conjugated Halides

Compound	Transition	Transition Moment (a.u.)
Trichloroethylene	$n \rightarrow \sigma^*$	0.0199
	$\pi \rightarrow \sigma^*$	0.0124
1,2-Dichloroethylene	$n \rightarrow \sigma^*$	0.0107
	$\pi \rightarrow \sigma^*$	0.0027

Chapter 5

A Simple Molecular Orbital Method for Computing σ and π Electronic Structures with Unificative Parameters

§1. Introductory Discussion

The simple LCAO MO method for discussing electronic structures of σ skeleton of unsaturated compounds has been developed by the present authors¹⁾ (hence which will be called σ MO method) and has been successfully applied to the discussion of some physicochemical properties of halogenated compounds^{2,3)} and of some aldehydes⁴⁾. In the method σ electrons are treated with an entirely new set of Coulomb and resonance energy parameters, part of which given in the A part of Table I. Because of these different sets of parameters for σ and π electron systems, comparison of σ and π electronic structures calculated is not direct.

And the new set of energy parameters for σ electron systems has a little conflict with that for π electron systems. When methylene and methyl groups in a molecule is treated by the σ MO method, the partial symmetry of the groups divides the secular equation into one symmetric part and one and two, respectively, antisymmetric parts. Antisymmetric parts being essentially π in nature, one of them

would come into conjugation with π electrons of the molecule, which is well known as hyperconjugation.⁵⁶⁾ In the σ MO method, hyperconjugation is not taken into account and its effect has been discussed by the ordinary LCAO MO method of π electron systems (hereafter referred to π MO method).

Calculated σ electron distribution by the σ method for imaginary $\text{CH}_3\dot{\text{C}}\text{HR}$ molecule (R is not taken into account) are shown in Table II where distributions are separated into each part of symmetry. Generally the calculated bond polarity of methyl and methylene groups are illustrated as follows:

	CH_3	CH_2
symmetric part	$\text{C} \leftarrow \text{H}$	$\text{C} \leftarrow \text{H}$
antisymmetric part 1	$\text{C} \rightarrow \text{H}$	$\text{C} \rightarrow \text{H}$
antisymmetric part 2	$\text{C} \rightarrow \text{H}$	
<hr/>		
total	$\text{C} \leftarrow \text{H}$	$\text{C} \leftarrow \text{H}$

where the arrow $\text{A} \leftarrow \text{B}$ corresponds to the polarity $\text{A}^{-\delta} \text{B}^{+\delta}$ and the larger arrow shows the larger polarity. Antisymmetric, that is, π parts show the polarity $\text{C} \rightarrow \text{H}$, which is in contrast with the following hyperconjugation treatment.

On the other hand from the hyperconjugation's standpoint, as is shown also in Table II, the polarity of the bond between

carbon and hydrogen pseudo- π orbital is such as $C \leftarrow H_3$ and $C \leftarrow H_2$.

This difference in polarity is due to the different set of Coulomb energy parameters. In the σ MO method from the upper part of Table I the Coulomb integral of the anti-symmetric part of the CH_3 carbon comes to be $\alpha - 0.38\beta$ and that of antisymmetric H_3 group orbital is $\alpha - 0.2\beta$, H_3 being more electronegative than C, while in the hyper-conjugation method such Coulomb integrals as $\alpha_{C\rho} = \alpha_{\pi} - 0.1/\beta\pi$ and $\alpha_{pseudo-\pi} = \alpha_{\pi} - 0.5/\beta\pi$ are popular, where pseudo- π orbital is more electropositive than the carbon π orbital.

It is pointed out by Mulliken et al.⁶⁾ in their paper on hyperconjugation that though the energy of hydrogen atom (-13.6 eV) itself is more negative than the energy of carbon $p\pi$ orbital (-11.2 eV), the energy of hydrogen pseudo- π orbital, which is expressed by

$$\alpha_{pseudo\pi} = \alpha_H - \frac{\gamma_{HH}}{1 - S_{HH}}$$

(γ_{HH} , S_{HH} : resonance integral and overlap integral, respectively,

between hydrogen orbitals in CH_3 and CH_2 group)

will be more positive than the energy of carbon $p\pi$ orbital.

Putting $\gamma_{HH} = -2.05$ eV and $S_{HH} = 0.26$, they obtained

$\alpha_{pseudo\pi} = -10.8$ eV. With the same integrals the energy

of the symmetric group orbital of hydrogens in methyl group is -16.3 eV, which is also more positive than the energy (-18.6 eV) of the symmetric hybridized (s^3p hybridized) orbital on the carbon. Thus for hyperconjugating methyl and methylene group such set of hyperconjugation parameters as $\alpha_{pseudo\pi} = \alpha_{\pi} - 0.5\gamma_{\pi}$, $\alpha_{Cp\text{ in }CH_3} = \alpha_{\pi} - 0.1\gamma_{\pi}$, $\gamma_{H_3-C} = 2.5\gamma$, $\gamma_{C-CH_3} = 0.7\gamma$ or a little modified one is often adopted,^{6,7)} where $\gamma = \alpha_{\pi} - S_{\pi\pi}\beta_{\pi}$.

Experimentally there would be no decisive facts whether $\alpha_{pseudo\pi}$ is more negative or more positive than α_{Cp} . Dipole moment and o,p- direction in electrophilic substitution of toluene seem to be well understandable not only in terms of hyperconjugative delocalization of electrons from H_3 to the ring but in terms of delocalization through symmetric part of σ MO's, as in the σ MO calculation, followed by change of Coulomb integral of the π orbital on the carbon atom attached to the methyl group (so-called inductive effect). In the present stage, however, it would be rational to follow such theoretical consideration as was done by Mulliken et al.

Though in most π MO computation of hyperconjugation large overlap integrals in methyl and methylene groups is taken into account, it has been made clear by the present

authors' discussion²⁾ that neglect of overlap integrals in carrying out σ MO calculation affects little on qualitative results of calculation.

In the present chapter the authors want to find a set of energy parameters by which σ and π electrons can be treated unificatively. But the parameters which have been used in the σ MO calculation are desired to be utilized here with as small modification as possible.

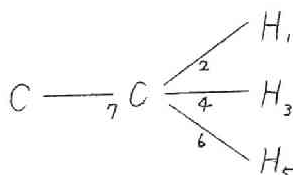
§2. Choice of New Set of Parameters

At first for the sake of clearness, we write down part of the secular determinant near a methyl group in the σ MO method.

$$\begin{array}{c|ccccccc}
 & 1 & 2 & 3 & 4 & 5 & 6 & 7 \\
 \hline
 1 & \alpha_H - E & \beta_{sp^3H} & 0 & 0 & 0 & 0 & 0 \\
 2 & \beta_{sp^3H} & \alpha_{sp^3} - E & 0 & \gamma & 0 & \gamma & \gamma \\
 3 & 0 & 0 & \alpha_H - E & \beta_{sp^3H} & 0 & 0 & 0 \\
 4 & 0 & \gamma & \beta_{sp^3H} & \alpha_{sp^3} - E & 0 & \gamma & \gamma \\
 5 & 0 & 0 & 0 & 0 & \alpha_H - E & \beta_{sp^3H} & 0 \\
 6 & 0 & \gamma & 0 & \gamma & \beta_{sp^3H} & \alpha_{sp^3} - E & \gamma \\
 7 & 0 & \gamma & 0 & \gamma & 0 & \gamma & \alpha_{sp^3} - E
 \end{array} \quad (1)$$

where $\gamma \equiv \beta_{sp^3}$ (one center).

The numbering of AO's is as follows:



It is separated into a symmetric part (S) and two degenerate antisymmetric part (A)*:

S:	(1,3,5)	(2,4,6)	7	
(1,3,5)	$\alpha_H - \epsilon$	β_{sp^3H}	0	
(2,4,6)	β_{sp^3H}	$\alpha_{sp^3} + 2\delta - \epsilon$	δ	
7	0	3δ	$\alpha_{sp^3} - \epsilon$	(2)

A:	(1,3,5)	(2,4,6)	
(1,3,5)	$\alpha_H - \epsilon$	β_{sp^3H}	
(2,4,6)	β_{sp^3H}	$\alpha_{sp^3} - \delta - \epsilon$	

Degenerate antisymmetric parts are nothing but what give the pseudo- π MO's, which are perpendicular to each other.

According to Mulliken⁶⁾ two resonance integrals---the one between hydrogens, β_{HH} , and the other between a hydrogen and a sp^3 hybridized orbitals that is directed to another

* In the notation of the group theory, methyl group belongs to C_{3v} symmetry and S corresponds to the irreducible representation A_1 and two A parts to E (doubly degenerate level).

hydrogen in the group, β'_{sp^3H} , becomes to be important. Then the secular determinant of methyl group would be, instead of Eqs. 2 and 3:

$$\begin{array}{c|ccc}
 \text{S:} & (1,3,5) & (2,4,6) & 7 \\
 \hline
 (1,3,5) & \alpha_H + 2\beta_{HH} - \epsilon & \beta_{sp^3H} + 2\delta & 0 \\
 (2,4,6) & \beta_{sp^3H} + 2\delta & \alpha_{sp^3} + 2\delta - \epsilon & \delta \\
 7 & 0 & 3\delta & \alpha_{sp^3} - \epsilon
 \end{array} \quad (4)$$

$$\begin{array}{c|ccc}
 \text{A:} & (1,3,5) & (2,4,6) & \\
 \hline
 (1,3,5) & \alpha_H - \beta_{HH} - \epsilon & \beta_{sp^3H} - \delta & \\
 (2,4,6) & \beta_{sp^3H} - \delta & \alpha_{sp^3} - \delta - \epsilon & \\
 \hline
 & & &
 \end{array} \quad (5)$$

where $\delta \equiv \beta'_{sp^3H}$

For methylene group antisymmetric parts are the same as Eq. 5 but the symmetric part is given as follows:

$$\begin{array}{c|ccc}
 \text{S:} & (1,3,5) & (2,4,6) & 7 \\
 \hline
 (1,3,5) & \alpha_H + \beta_{HH} - \epsilon & \beta_{sp^3H} + \delta & 0 \\
 (2,4,6) & \beta_{sp^3H} + \delta & \alpha_{sp^3} + \delta - \epsilon & \delta \\
 7 & 0 & 2\delta & \alpha_{sp^3} - \epsilon
 \end{array} \quad (6)$$

Now we are going to reestimate a new set of parameters.

Coulomb integrals of various hybridized orbitals of carbon and one-center resonance integrals between hybridized

orbitals will be derived from the parameters α_{sp^2} and $\beta_{sp^2-sp^2}$ (one center). In the simplest approximation where electronic interaction is neglected, the Coulomb integral of $s^m p^{l-m}$ hybridized orbital is written as follows:

$$\alpha_{s^m p^{l-m}} = m\alpha_s + (l-m)\alpha_p \quad (7)$$

And the resonance integral between $s^m p^{l-m}$ hybridized orbitals both on the same carbon atom is

$$\beta_{s^m p^{l-m}-s^m p^{l-m}} \text{ (one center)} = m(\alpha_s - \alpha_p) \quad (8)$$

From these equations and the settled parameters ($\alpha_{sp^2} = \alpha$ and $\beta_{sp^2-sp^2}$ (one center) = $0.38/\beta$) are derived the parameters in the line B of Table I.

The most important parameter that decides contributions of σ and π components is the resonance energy between the hydrogen atoms (β_{HH}) in methyl or methylene group.

The overlap integral between carbon sp^2 hybridized orbitals in a bond (at 1.34 \AA) is 0.77, while the overlap integral between hydrogens in CH_3 or CH_2 group is $0.26^{(6)}$. If we simply consider that the resonance integral is proportional to the overlap integral, β_{HH} would be $\beta_{HH} = \beta_{sp^2-sp^2} \times S_{HH}/S_{sp^2-sp^2} = \beta \times 0.26/0.77 = 0.34\beta$. But for this value the Coulomb integral of hydrogen atoms in the

symmetric part, $\alpha_H + 2\beta_{HH} = \alpha - 0.2\beta - 2 \times 0.34\beta = \alpha + 0.48\beta$, becomes more negative than that of the carbon hybridized orbital, $\alpha_{sp^3} - 2\delta \equiv \alpha_{sp^3} = \alpha + 0.475\beta$, which leads to such contribution as C→H to the bond polarity. This contribution seems to be contradictory to chemical experiences that methyl group shows an electron-repelling inductive effect as well as hyperconjugation effect. In order to make the Coulomb integrals of hydrogens more positive than those of the carbon in both the symmetric and the antisymmetric parts the range $0.3\beta < \beta_{HH} < 0.2\beta$ seems to be appropriate. The limit 0.2β is set according to the similar discussion on the antisymmetric part. In the present chapter $\beta_{HH} = 0.25\beta$ is adopted tentatively.

As to another resonance integral, β'_{sp^3-H} , on the basis of the overlap integrals, $S_{sp^3-H} = 0.69$ and $S'_{sp^3-H} = 0.15$, and on the assumption of the proportionality of these two kind of integrals, β'_{sp^3-H} is estimated to be 0.3β . In the present chapter 0.5β is adopted instead of 0.3β , because the smaller (in magnitude) value leads to the result that the lowest unoccupied σ level in the compounds we treated gets nearer (or even lower in the worst case) than the lowest unoccupied π level, which seems to be irrational from the point of view of spectroscopic experiences.

Estimation of the resonance integral between carbon $2p$ π orbitals of a double bond, $\beta_{\pi\pi}$, is now necessary for our purpose that one can calculate σ and π electronic systems in an unificative set of parameters. Though from the overlap integrals, $S_{sp^2-sp^2} = 0.77$ and $S_{\pi\pi} = 0.25$ and the proportionality, $\beta_{\pi\pi} = \beta \times 0.25 / 0.77 = 0.32 \beta$ is obtained, we used a little smaller (in magnitude) value $\beta_{\pi\pi} = 0.28 \beta$, for the latter is preferred in connection with the energies of the lowest unoccupied π and σ levels. This choice would not be irrational comparing the experimentally deduced values of the integrals $\beta_{\pi\pi} = \text{ca. } -2.2 \text{ eV}^{7)}$ and $\beta_{sp^2-sp^2} = -6.9 \text{ eV}^{3)}$. The integral $\beta_{\pi\pi}$ of the $C_\alpha - C_\beta$ bond in the $-C_\beta - C_\alpha \equiv H_3$ part is set to be 0.20β , in accord with the ratio (the resonance integral between π orbitals in $C_\alpha - C_\beta$) / (that in the normal π bond) $= 0.7$ which has been often used in the hyperconjugation treatment.⁶⁾ Thus the new set of parameters in Table I is obtained.

The secular determinants Eqs. 4, 5 and 6 have the following numerical forms:

CH₃S:

	$\alpha + 0.3\beta - \epsilon$	1.93β	0	
	1.93β	$\alpha + 0.475\beta - \epsilon$	0.285β	(9)
	0	0.855β	$\alpha - 0.095\beta - \epsilon$	

CH₂S:

	$\alpha + 0.05\beta - \epsilon$	1.43β	0	
	1.43β	$\alpha + 0.19\beta - \epsilon$	0.285β	(10)
	0	0.57β	$\alpha - 0.095\beta - \epsilon$	

A:

	$\alpha - 0.45\beta - \epsilon$	0.43β		(11)
	0.43β	$\alpha - 0.38\beta - \epsilon$		

One of the antisymmetric parts in a molecule, as an instance in propylene, that is, π part which is in conjugation with π orbitals in ethylene bond will be given explicitly here (Eq. 12):

	H_3	\equiv	C	$—$	C	$=$	C	
$H,$	$\alpha' - 0.07\beta - \epsilon$		0.43β		0		0	
\equiv								
C	0.43β		$\alpha' - \epsilon$		0.20β		0	
$ $								
C	0		0.20β		$\alpha' - \epsilon$		0.28β	(12)
$ $								
C	0		0		0.28β		$\alpha' - \epsilon$	

in order to compare the secular determinant of the same molecule in the hyperconjugation treatment. (Eq. 13):

$$\begin{array}{c|ccccc}
 \begin{array}{c} \text{H}_3 \\ | \\ \text{C} \\ | \\ \text{C} \\ | \\ \text{C} \end{array} & \begin{array}{c} \text{H}_3 \\ \equiv \\ \alpha_0 - 0.5\beta_0 - \epsilon \\ 2.5\beta \\ 0 \\ 0 \end{array} & \begin{array}{c} \text{C} \\ 2.5\beta \\ \alpha_0 - 0.1\beta_0 - \epsilon \\ 0.7\beta \\ 0 \end{array} & \begin{array}{c} - \\ \text{C} \\ 0 \\ 0.7\beta \\ \alpha_0 - \epsilon \\ \beta \end{array} & \begin{array}{c} = \\ \text{C} \\ 0 \\ 0 \\ \beta \\ \alpha_0 - \epsilon \end{array} \\
 & & & & (13)
 \end{array}$$

where α_0 and β_0 are the Coulomb integral of a carbon π orbital and the resonance integral between carbon π orbitals in a normal π bond, respectively. Though the unit is different in Eqs. 12 and 13, the both seems to result in similar electron distributions and similar energy configurations.

Thus we can treat unificatively both σ and π electronic structures with one set of parameters.

§3. Calculated Results and Discussion

Electron distributions and molecular orbitals calculated by the new set of unificative parameters for $\text{CH}_3\dot{\text{C}}\text{HR}$ radical are grouped into σ (symmetric), π (antisymmetric and conjugating with π electrons) and π' (antisymmetric and perpendicular to the π part) parts and illustrated in Table II. As one can see in the figures the calculated bond polarity of each part in methyl group is:

symmetric part	$\text{C} \leftarrow \text{H}$
antisymmetric part 1	$\text{C} \leftarrow \text{H}$
antisymmetric part 2	$\text{C} \leftarrow \text{H}$
<hr/>	
total	$\text{C} \leftarrow \text{H}$

The direction of polarity of each part seems to agree with our chemical intuitions.

In Fig. 2 are illustrated σ , π and π' electron distributions of toluene calculated by the present method. Direction of polarity of each part is the same as shown in $\text{CH}_3\text{CH}\cdot\text{R}$.

In this chapter though some new parameters are added to those previously settled in the σ MO method, some uncertainties seem to remain to exist--especially in estimating the resonance integral between hydrogens. In this connection such discussion as Morita's suggestive ASMO discussion⁸⁾ on the hyperconjugation of toluene would be necessary.

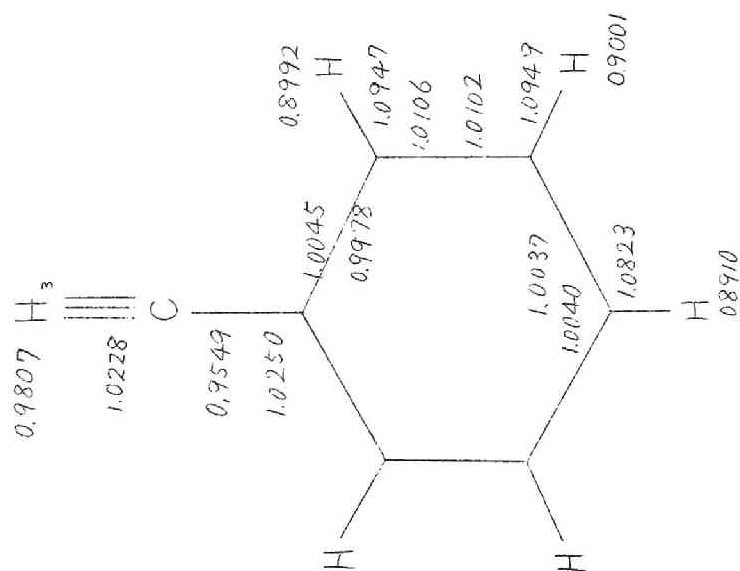
Interaction of σ and π electrons, so-called $\sigma-\pi$ interaction; is not included in the treatment in this chapter. This unificative method, however, would ~~enable~~^{enable} us to take the $\sigma-\pi$ interaction into account in a simplest form.

Reference

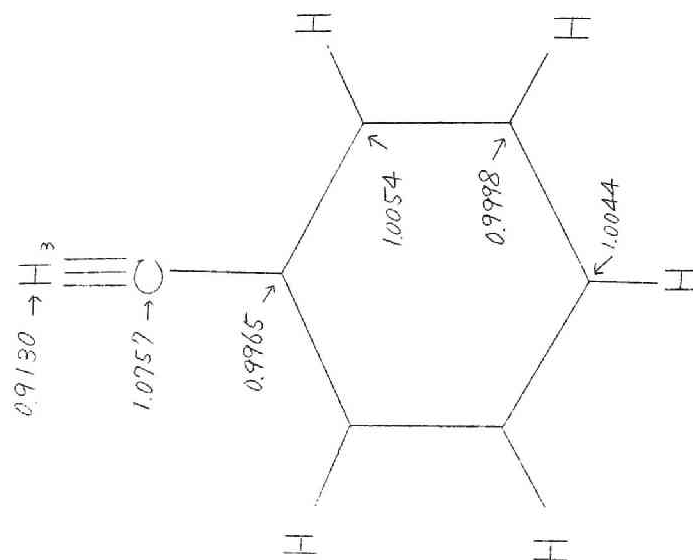
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Table I Set of Unificative Energy Parameters

	Coulomb Integrals	Resonance Integrals
(A) Parameters Already Settled	$\alpha_{sp^2} = \alpha$ $\alpha_H = \alpha - 0.2\beta$	$\beta_{sp^2-sp^2} = \beta$ (bonding) $\delta = 0.38\beta$ (one center) $\beta_{sp^2-sp^3} = 0.92\beta$ $\beta_{sp^2-H} = 0.94\beta$ $\beta_{sp^3-H} = 0.93\beta$
(B) Parameters Derived from Those in (A)	$\alpha_s = \alpha + 0.76\beta$ $\alpha_{sp} = \alpha + 0.475\beta$ $\alpha_{sp} = \alpha + 0.19\beta$ $\alpha_{sp^3} = \alpha - 0.095\beta$ $\alpha_p = \alpha - 0.38\beta$	$\beta_{sp^3-sp^3} = 0.285\beta$ (one center)
(C) Parameters Settled Now		$\beta_{HH} = 0.25\beta$ (in CH_3) $\beta_{sp^3-H} = 0.5\beta$ (H in CH_3 ; sp^3 in CH_3 but not directed to the H) $\beta_{\pi\pi} = 0.28\beta$ (bonding) $\beta_{\pi\pi} = 0.20\beta$ (bonding between C- CH_3)



a) Symmetric (σ) Part



b) Antisymmetric (π) Part

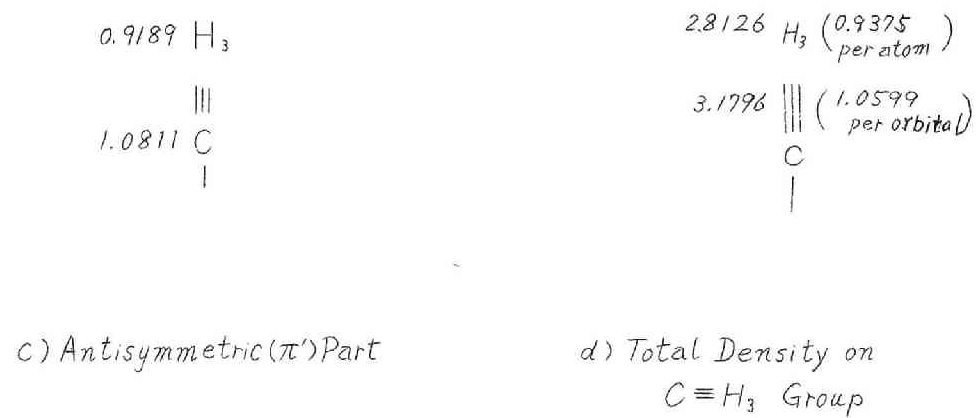


Fig. 2 Electron distribution of toluene calculated by the present method

Table II. Comparison of Electron Distribution by Three Methods*

Method	Symmetry	H ₂ ≡ ≡ ≡ ≡ ≡ C			C ————— H		
					σAO	πAO	σAQ
σ Method	S	.6670	1.3212	.9483	1.0669		.8968
	A	1.0963 x2	.9037 x2				
	total	2.8596 (.9532)	3.1286 1.0429)	.9483	1.0669		.8968
Hyper- conjugation Method (π Method)		.9094	1.0695			1.0211	
This Method	S	.9618	1.0456	.9598	1.0385	1.1006	.8937
	A(π)	.9073	1.0604			1.0323	
	A(π')	.9189	1.0811				
	total	2.7880 (.9293)	3.1871 1.0624)	.9598	1.0385 1.0323	1.1006	.8937

* Numbers in parentheses are electron density on each atom.

Chapter 6

Electronic Spectra and Some Physicochemical Properties of Anthracene

§1. Introduction

Electronic spectra of anthracene have been theoretically studied by LCAO ASMO SCF CI (linear-combination-of-atomic-orbital antisymmetrized molecular orbital of self-consistent field and with configuration interaction) method by Mataga et al.¹⁾ They used an approximation that the Coulomb repulsion integrals were written in the form $\gamma_{\mu\nu} = 14.39 / (r_{\mu\nu} + a)$ eV and also that the Coulomb penetration integrals were entirely neglected, where a is a constant dependent on the atoms μ and ν .

As one can see in Chapter 3 of Part I, we made an LCAO ASMO SCF calculation on the anthracene, getting SCF ground state molecular orbitals. The method of estimation of the Coulomb repulsion integrals was that by Pariser and Parr.²⁾ We took the Coulomb penetration integrals into account based on the theoretical calculation.³⁾

In the present chapter, using the results (SCF MO's) in that chapter, we are going to give a few brief discussions on the ionization potential and on the calculated bond orders and the observed bond distances, and to make an LCAO

ASMO SCF CI calculation on electronic spectra of anthracene.

§2. Ionization Potential

Ionization potential I is given by the following equation⁴⁾:

$$I = - (W_{2p} + \varepsilon_7) \quad (1)$$

Putting $W_{2p} = -11.28 \text{ eV}^2)$ and $\varepsilon_7 = -0.2930 \text{ eV}$ from Table I of Chapter 3 of Part I, we obtain 11.57 eV. as the first ionization potential of anthracene, which is, though no experimental results are available, much larger than the estimated value, 7.23 eV., by Matsen⁵⁾. Giving too large calculated value is not particular to the case of anthracene, but the general tendency of SCF calculation⁶⁾: On this point Stewart⁷⁾ made a discussion concluding that the assumption

$$H \chi_{2p} = W_{2p} \chi_{2p} \quad (3)$$

was not actually satisfied. In Eq. 3, χ_{2p} is the 2p orbital on carbon atom and H is one electron hamiltonian.

§3. Bond Order and Bond Distance

Our SCF bond orders and observed bond distances are collected in Table I, in comparison with the SCF bond orders by Pritchard and Sumner in a rough approximation^{8)*} and with the bond orders in simple LCAO treatment. It is seen in Table I that SCF bond orders in the present calculation are parallel with the observed bond distances except for the bond 11--12, in accordance with Pritchard and Sumner's result. The discrepancy in the bond 11-12 seems to indicate that the bond order of a bonding is not determined only by its length but by its nature; namely, whether the ending carbons of this bonding are primary, secondary or tertiary.

§4. Electronic Spectra

The energies of configurations, the values of inter-configurational matrix elements and wave functions of the excited states are listed in Table II, where only four lower excitations are considered. The calculated excitation energies and oscillator strengths are given in Table III, together with the observed values. The agreement with experiments is

* As to this approximation, see Footnote on p. 46 of this thesis.

good, but for the inversion of excitation energies of ${}^1B_{2u}^-$ band and ${}^1B_{3u}^+$ band, which will be improved by the inclusion of more possible configurations.

In Fig. 1 calculated and observed excitation energies are graphically illustrated. Difference with Mataga's result is not serious.

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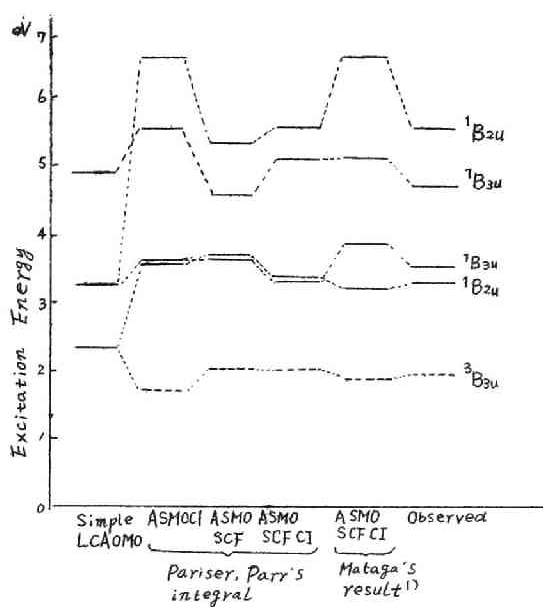


Fig. 1 Calculation of excitation energy of anthracene

Table I. The Bond Orders and Observed Bond Distances of Anthracene

Bond	Bond order			Obsd. bond distances (\AA) ^{b)}
	Present treatment	Pritchard and Sumner ^{a)}	Simple LCAO	
1-2	0.8347	0.8422	0.7374	1.370
9-11	0.6107	0.6318	0.6061	1.396
2-3	0.4542	0.4493	0.5859	1.408
1-11	0.4383	0.4178	0.5354	1.423
11-12	0.5533	0.5484	0.4849	1.436

a) Ref. 8.

b) Ref. 9.

Table II The Energies of Configurations, The Values of Interconfigurational Matrix Elements and the Excited States Wave Functions^{a)}

$B_{2u} :$	$[66 99] = 5.535,$	$[69 96] = 0.551,$
	$[77 88] = 5.419,$	$[78 87] = 0.885.$
	$E(V_{78}) - E_0 = 3.782,$	$E(V_{69}) - E_0 = 5.206,$
	$E(T_{78}) - E_0 = 2.013,$	$E(T_{69}) - E_0 = 4.104.$
	$[67 89] = -0.094,$	$[69 87] = 0.369.$
	$\langle V_{78} V_{69} \rangle = 0.833,$	$\langle T_{78} T_{69} \rangle = 0.094.$
	$\Psi(^1B_{2u}^-) = 0.908 V_{78} - 0.418 V_{69},$	
	$\Psi(^1B_{2u}^+) = 0.418 V_{78} + 0.908 V_{69},$	
	$\Psi(^3B_{2u}^-) = 0.999 T_{78} - 0.045 T_{69},$	
	$\Psi(^3B_{2u}^+) = 0.045 T_{78} + 0.999 T_{69},$	
$B_{3u} :$	$[66 88] = 5.145,$	$[68 86] = 0.348,$
	$[77 99] = 5.198,$	$[79 97] = 0.502.$
	$E(V_{77}) - E_0 = 3.743,$	$E(V_{68}) - E_0 = 4.684,$
	$E(T_{77}) - E_0 = 2.740,$	$E(T_{68}) - E_0 = 3.987.$
	$[76 89] = -0.094,$	$[79 86] = -0.415.$
	$\langle V_{77} V_{68} \rangle = -0.736,$	$\langle T_{77} T_{68} \rangle = 0.094.$
	$\Psi(^1B_{3u}^+) = 0.877 V_{77} + 0.480 V_{68},$	
	$\Psi(^1B_{3u}^-) = 0.480 V_{77} + 0.877 V_{68},$	
	$\Psi(^3B_{3u}^-) = 0.997 T_{77} - 0.075 T_{68},$	
	$\Psi(^3B_{3u}^+) = 0.075 T_{77} + 0.997 T_{68},$	

a) In units of eV.

Table III. The Excitation Energies and the Oscillator Strengths of Anthracene

Symmetry	Excitation energy(eV)			Oscillator strength	
	Calcd. (with CI)	Calcd. (without CI)	Obsd.	Calcd. (with CI)	Obsd.
$^1B_{2u}^-$	3.40	3.78	3.30 ^{a)}	0.15	0.1 ^{a)}
$^1B_{3u}^+$	3.34	3.74	3.50 ^{a)}	0.20	0 ^{a)}
$^1B_{3u}^-$	5.09	4.68	4.80 ^{a)}	1.94	2.20 ^{a)}
$^1B_{2u}^+$	5.59	5.21	5.64 ^{a)}	1.01	0.65 ^{a)}
$^3B_{2u}^-$	2.01	2.01	1.8 ^{b)}	0.00	—
$^3B_{3u}^-$	2.73	2.74	—	0.00	—
$^3B_{3u}^+$	3.99	3.99	—	0.00	—
$^3B_{2u}^+$	4.11	4.10	—	0.00	—

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Chapter 7

A Simple Molecular Orbital Method for Discussing Electronic Structures of Stereoisomers — Theoretical Method and ESR Hyperfine Splittings of Terephthalaldehyde Anion

§1. Introduction

Differences of properties of stereoisomers of organic compounds have long excited the interests of chemists in their chemical reactivities, physical properties, spectroscopic data, and so forth.

From the point of view of molecular orbital (MO) treatment stereoisomers may be divided into two classes: one consisting of geometrical (cis- and trans-) and rotational (gauche- and trans-) isomers and the other containing optical isomers. In the following, discussions would be limited to the isomers of the first class.

Electronic structures of these isomers are calculated to be identical in the scope of the simple LCAO MO method in which electronic interactions are formally neglected, for in this method the secular equation of one of the isomers is equal to that of the other. To the discussion on the difference in energy of the first class stereoisomers, a

classical electrostatic calculation has been useful as well as the ASMO (anti-symmetrized MO) calculation including electronic interactions. To the discussion on their electron distribution the ASMO SCF (self-consistent field) calculation would be necessary and adequate; a typical example would be the strict calculation of π electron distribution of trans- and cis-butadiene by Parr and Mulliken.¹⁾ In non-polar compounds such as butadiene, indeed, such a strict but very troublesome calculation would be indispensable in order to show any difference of distribution. But in a compound containing polar groups in it some differences of electron distribution between the isomers, which may be sufficient for a qualitative comparison, would be obtained by a simple LCAO MO method with parameters modified by considering electronic interactions between polar groups.

In this chapter such a modified simple molecular orbital method is to be settled for conjugated molecules and is to be applied to the interesting differences of the proton hyperfine couplings in ESR (electron spin resonance) spectroscopy between terephthalaldehyde anion isomers recently investigated by Maki²⁾.

As to the structural isomers, electronic structures are of course different even in the simple LCAO MO

calculation. In this simple method, however, it is difficult to take into account the effects of near-by polar groups sufficiently, while actually the electronic interactions would cause a considerable change in the electron distribution. The simple MO method with modified parameters that is utilized for geometrical isomers would be of use also for this class of isomers. Applications to actual problems—nuclear coupling constants and asymmetric parameters in PQR (pure nuclear quadrupole resonance) spectra, dipole moments, etc.—of structural isomers will be given in the future.³⁾

§2. Theoretical Method

In the Hückel MO theory, by solving the secular equation

$$\sum_{s=1}^n (a_{rs} - \lambda_i \delta_{rs}) C_{is}^{\pi} = 0 \quad (r=1, 2, \dots, n) \quad (1)$$

molecular orbitals are obtained as a linear combination of atomic orbitals (AO's) as follows:

$$\psi_i^{\pi} = \sum_{r=1}^n C_{ir}^{\pi} \chi_r^{\pi} \quad (i=1, 2, \dots, n) \quad (2)$$

where n is the number of π AO's, χ_r^{π} is the r th π AO's, C_{ir}^{π} is the coefficient of the r th AO in i th MO, λ_i is the i th eigenvalue of Eq. 1, and a_{rr}° and a_{rs}° are the parameters standing for the Coulomb integral of the r th

AO and the resonance integral between the r th and the s th AO's, respectively.

The molecular orbitals of σ electrons are similarly calculated as a linear combination of σ atomic orbitals (sp^2 or sp^3 hybridized orbitals on carbon atoms, hydrogen $1s$ orbitals and σ atomic orbitals on substituents)^{4)-6)*}:

$$\psi_j^\sigma = \sum_{t=1}^N C_{jt}^\sigma \chi_t^\sigma \quad (j = 1, 2, \dots, N) \quad (3)$$

with parameters b_{tt}^σ and b_{tu}^σ defined as

$$\left. \begin{array}{l} \text{Coulomb integral} \quad \alpha_t^\sigma = b_{tt}^\sigma \beta_\sigma + \alpha_\sigma \\ \text{resonance integral} \quad \beta_{tu}^\sigma = b_{tu}^\sigma \beta_\sigma \end{array} \right\} \quad (4)$$

where N the number of σ AO's and β_σ is the resonance integral of the standard C-C σ bond of benzene. From these MO's the π and the σ electron densities, q_r^π and q_t^σ , respectively, are calculated

$$\left. \begin{array}{l} q_r^\pi = \sum_{i=1}^{\pi} \nu_i^\pi (C_{ir}^\pi)^2 \\ q_t^\sigma = \sum_{j=1}^N \nu_j^\sigma (C_{jt}^\sigma)^2 \end{array} \right\} \quad (5)$$

where ν_i represents the number of electrons in the i th MO.

Suppose that q_r^π and q_t^σ have already been calculated by the use of assumed parameters. We call them the densities and the parameters, respectively, of the zero order. Of

course the results are identical with respect to cis- and trans- isomers. If the compound has even number of electrons (closed shell), Fock's operator of the p th atomic orbital on the A th atom, with electron-electron interaction, which corresponds to the Coulomb integral in the simple MO treatment, would be given as follows:⁷⁾

$$F_{pp} = W_p(q_p) + \frac{1}{2} q_p \gamma_{pp} + (Z_A - 1) \xi_{pA} + \sum_{\substack{r \\ (\text{on } A)}}^{\text{all AOs}} q_r \gamma_{pr} \quad (6)$$

$$+ \sum_{\substack{r \\ (\text{not on } A)}}^{\text{all AOs}} q_r \gamma_{pr} + \sum_{\substack{B \\ (\neq A)}}^{\text{all cores}} Z_B \xi_{pB}$$

The former four terms are concerned with the electrons and the core on the atom A, and the latter two represent the interactions with electrons and cores on the other atoms; and γ_{pr} and ξ_{pB} are the electron repulsion integral and the electron core attraction integral, respectively, which are represented by

$$\gamma_{pr} = \int \chi_p^*(1) \chi_p(1) \frac{e^2}{r_{12}} \chi_r^*(2) \chi_r(2) d\tau_1 d\tau_2$$

$$\xi_{pB} = - \int \chi_p^*(1) \frac{e^2}{r_{1B}} \chi_p(1) d\tau_1$$

and γ_{pp} and ξ_{pA} are the corresponding one-center integrals, and Z_B is the charge of the core B. $W_p(q_p)$ is the energy of an electron on the p th AO in its valence state, which is a function of the electron density q_p .

If one assumes that when the γ th and the γ th AO's

belong to the same atom B, wherever each of them may be directed, $\gamma_{p\gamma}$ is equal to $\gamma_{p\delta}$ and further that ξ_{pB} is equal to them (hereafter they are designated by γ_{AB}), then the latter two terms are written as follows:

$$- \sum_{\substack{B \\ (\neq A)}} Q_B \gamma_{AB} \quad (8)$$

where Q_B is the net charge on the atom B

$$Q_B = Z_B - \sum_{\substack{\text{all } A\delta\delta \\ \gamma \\ (\text{on } B)}} q_{\delta\gamma} \quad (9)$$

The assumption would be acceptable in this simple qualitative discussion. As W_p becomes more positive and $-\frac{1}{2} q_{pp}$ more negative when q_{pp} is set larger, the sum

$$W_p^o = W_p - \frac{1}{2} q_{pp} \gamma_{pp} - \xi_{pA} \quad (10)$$

might be independent of the density*. Thus, the rest of the former terms is reduced to

$$- Q_A \gamma_{AA} \quad (11)$$

And a simple expression

$$F_{pp} = W_p^o - \sum_{\delta}^{\text{all atoms}} Q_B \gamma_{AB} \quad (12)$$

* In stereoisomers the assumption expressed by Eq. 10 is unnecessary. The assumption is needed only in structural isomers.

is obtained, W_p° being a constant depending only on the kind and the hybridization of the atom (sp^2 carbon, sp^3 carbon, hydrogen and so forth). We choose a certain atom of a kind as the standard, putting 0 on the shoulder as follows:

$$F_{gg}^\circ = W_g^\circ - \sum_{\substack{\text{all atoms} \\ g}} Q_B Y_{gB} \quad (13)$$

At this stage we return to the simple LCAO MO treatment, regarding the F_{pp} as the new Coulomb integral α_p modified with electronic interactions, and F_{gg}° as the standard integral α_g° assumed to be equal to that of the zero order (Eqs. 1 and 4). Then the new Coulomb integrals for π electrons are

$$\left. \begin{aligned} \alpha_g^\circ &= \alpha_\pi + a_{gg}^\circ \beta_\pi \\ \alpha_p &= \alpha_p^\circ + (F_{pp} - F_{gg}^\circ) \end{aligned} \right\} \quad (14)$$

or the new parameters a_{pp}' and a_{gg}' are

$$\left. \begin{aligned} a_{gg}' &= a_{gg}^\circ \\ a_{pp}' &= a_{pp}^\circ + (F_{pp} - F_{gg}^\circ) / \beta_\pi \end{aligned} \right\} \quad (15)$$

Also for σ electrons

$$\left. \begin{aligned} b_{gg}' &= b_{gg}^\circ \\ b_{pp}' &= b_{pp}^\circ + (F_{pp} - F_{gg}^\circ) / \beta_\sigma \end{aligned} \right\} \quad (16)$$

With these new parameters of the first order, which are of course different between two geometrical isomers, are calculated π and σ electron distributions of the first order, showing the difference between the isomers.

Instead of Eqs. 15 and 16, Eq. 17

$$\left. \begin{aligned} a_{pp'} &= a_{pp}^{\circ} + k (F_{pp} - F_{qq}^{\circ}) / \rho_{\pi} \\ b_{pp'} &= b_{pp}^{\circ} + k (F_{pp} - F_{qq}^{\circ}) / \rho_{\sigma} \end{aligned} \right\} \quad (17)$$

would be better used. The value of k is unity in the Eqs. 15 and 16 but this value might lead to over-estimation of the effects, and so as to get nearer to the self-consistency, k might be better settled as $0 < k < 1$.

§3. ESR Hyperfine Splittings of Terephthalaldehyde Anion

Recently an ESR spectrum of terephthalaldehyde mono-negative ion radical produced by the electrolytic reduction of the aldehyde has been observed by Maki²⁾ and it has been found that the hyperfine splittings of the spectrum cannot be interpreted without taking them as rising from two radical species, each of which has three pairs of protons with the coupling constants, species A: 2.08, 0.70 and 3.89 gauss and species B: 1.54, 1.16 and 3.81 gauss. He regarded them

as cis- and trans-isomers of the anion radical distinguished in the ESR spectrum because of the restricted rotation of the aldehyde groups and they suggested that the species A would be the cis isomer, whereas B the trans isomer.

It would be interesting to apply the method developed in the preceding paragraph and to see which species is assigned to which isomer and furthermore which coupling constant to which proton.

As terephthalaldehyde anion is a radical, Fock's operator in the radical is a little different from Eq. 6.⁸⁾ In this qualitative discussion, however, the simplified expression, Eq. 12, would be rationally adopted even for a radical and thus no special notice to being open shell is not paid in this paragraph.

Evaluation of Atomic Integrals.--Electron repulsion integrals necessary to the evaluation of Fock's operator are estimated in the form as used by Mataga⁹⁾ as follows:

$$\gamma_{AB} = \frac{14.39}{a_{AB} + \gamma_{AB}} \text{ eV} \quad (17)$$

where a_{AB} is the distance in Å from the atom A to B and is a constant settled so as to fit experimental values at $\gamma_{AB}=0$ (ionization potential minus electron affinity) if A and B are atoms of the same kind. When A and B are of different

kind, an arithmetical mean may roughly be adopted. The values of a_{AB} are tabulated in Table I.

Values of β_π and β_σ , standard resonance integrals, are taken as follows:

$$\left. \begin{aligned} \beta_\pi &= -2.5 \text{ eV} \\ \beta_\sigma &= -8.0 \text{ eV} \end{aligned} \right\} \quad (18)$$

and k is set unity.

The geometry of the aldehyde and its anion are considered to be planar with bond lengths of 1.40 Å for C-C (aromatic), 1.52 Å for C-C (substituent), 1.08 Å for C-H and 1.22 Å for C=O and with all bond angles of 120°.

Parameters of the Zero Order--Parameters of the zero order for π and σ electron systems are collected in Table II. The values of $a_{rr'}$ and $a_{rs'}$ for π electron systems are similar to those used popularly. As to the σ system values in the Table, except for O and C=O, are taken from the recent paper by the authors.⁶⁾ The values of $a_{oo'}$ and $a_{co'}$ are settled anew by referring to the ionization potentials and electron affinities of oxygen, and to the bond energy of the C-O single bond of alcohols or ethers and the ratio of the overlap integrals for C=O and C-O bonds, respectively.

Electron Distributions of the Zero Order--In the Fig. 1 are given electron distributions calculated with the parameters of the zero order. Since it is needless to say that results are identical for both isomers, the patterns for only the cis-isomer are written in the figure.

Parameters of the First Order--By using the net charge of the anion given in the Fig. 1 and the integrals of γ_{AB} , β_{π} and β_{σ} given in the foregoing section, new parameters of the first order are derived.

As for the π electron system, as the circumstances affecting π AO's C_{II} and C_{III} are invariant of the isomerism, their $a_{rr'}$'s are taken equal to a_{rr^0} 's.* For carbons IV and V, which are indistinguishable in the zero order, new parameters are estimated by looking on tentatively the C_V π AO in the trans isomer as a standard; and for oxygens, the O_I π AO in the trans isomer as a standard.

Similar standardization and recalculation of the parameters are carried out also for σ AO's. The values of parameters $a_{rr'}$ and $b_{tt'}$ of the first order thus calculated for both isomers are tabulated in Table III.

Results and Discussion--Pi and Sigma electron densities and π spin density of the isomers of terephthalaldehyde

* As to the numbering of π AO's, see Fig. 1

anion are calculated with the parameters of the first order; the results are given in Fig. 2.

As would be expected from a simple electrostatic consideration, in both isomers π electron density on C_V is larger than that on C_{IV} , since to the latter the electron rich and accordingly repulsive center of oxygen is located nearer. Similar tendency is found to appear also in σ electron densities on ring hydrogens and ring carbons. The π spin density is calculated as the density of the half-occupied level of the anion.

In order to compare with the calculation, experimental proton hyperfine coupling constants, a_H , are converted into spin densities on the adjacent carbon, ρ_C , with the equation

$$a_H = Q\rho_C \quad (19)$$

where the constant Q is equal to -23 gauss.¹⁰⁾ Strictly speaking, the constancy of Q would not hold in this case, for the different polarity of each C-H bond, as is seen in Fig. 2, would yield a different value of Q , but in a qualitative discussion like this such a slight difference would be of little significance.

On collating calculated spin densities with experimental

ones indicated in Table IV, we find their good mutual agreement, obtaining the following assignments:

(1) The species A is the cis isomer and the species B is the trans isomer, in agreement with Maki's proposition.

(2) In each isomer the largest (in absolute value) and nearly invariant coupling constant is originated from the aldehyde proton.

(3) In the trans isomer the order of the spin density on ring carbons is $C_V > C_{IV}$. On the other hand in the cis isomer the spin density on C_{IV} is much larger than that on C_V . This result seems very interesting because the order of the spin density is inverse to that of total π electron density and is contradictory to a simple electrostatic presumption. On inspecting the calculated electron distribution of each molecular orbital (Table V), such a presumption seems to be warrantable to the total density and to the distribution of molecular orbitals of lower energy, but not necessarily to that of molecular orbitals of higher energy or of less bonding or antibonding nature, as the half-occupied orbital of the anion discussed here.

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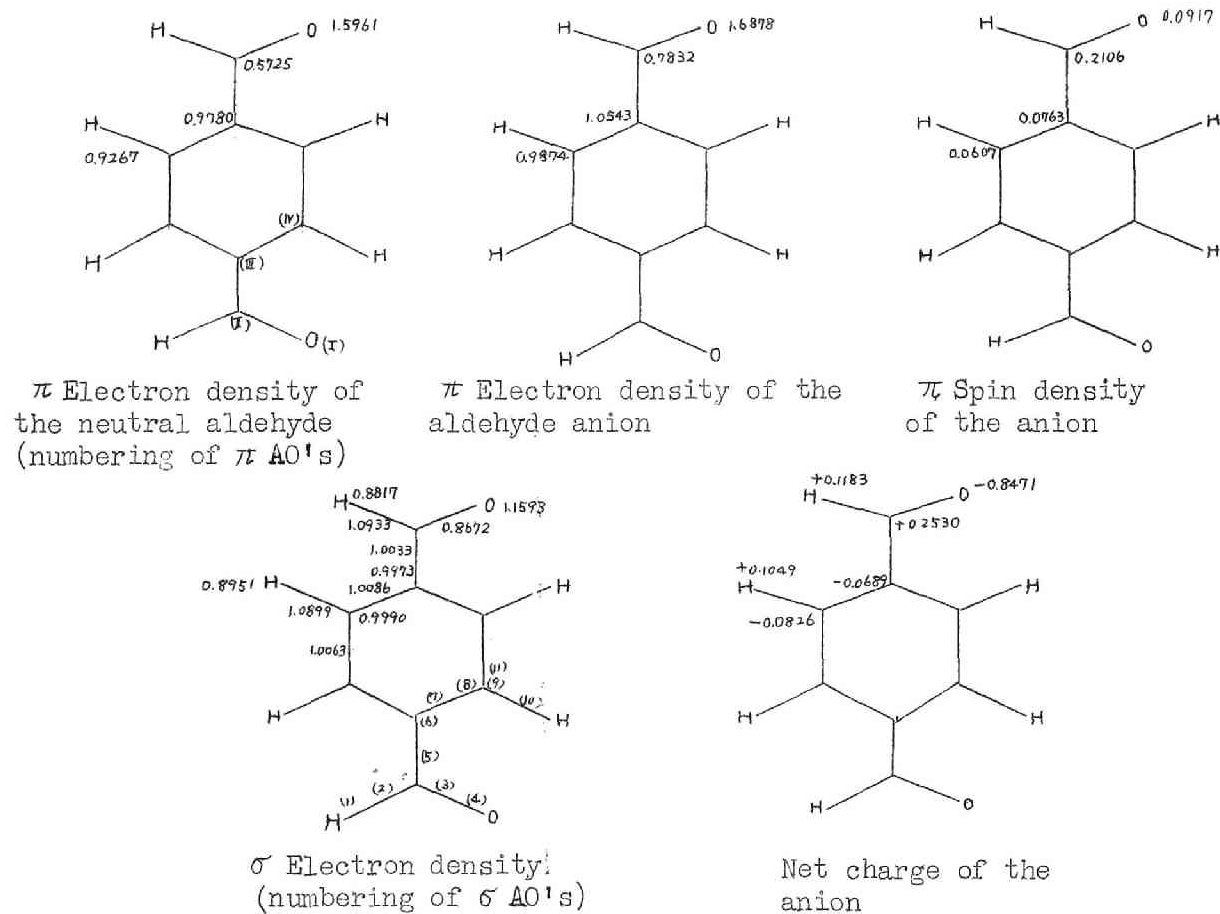


Fig. 1 Electron distributions of the zero order (numbering of AO's in parentheses)

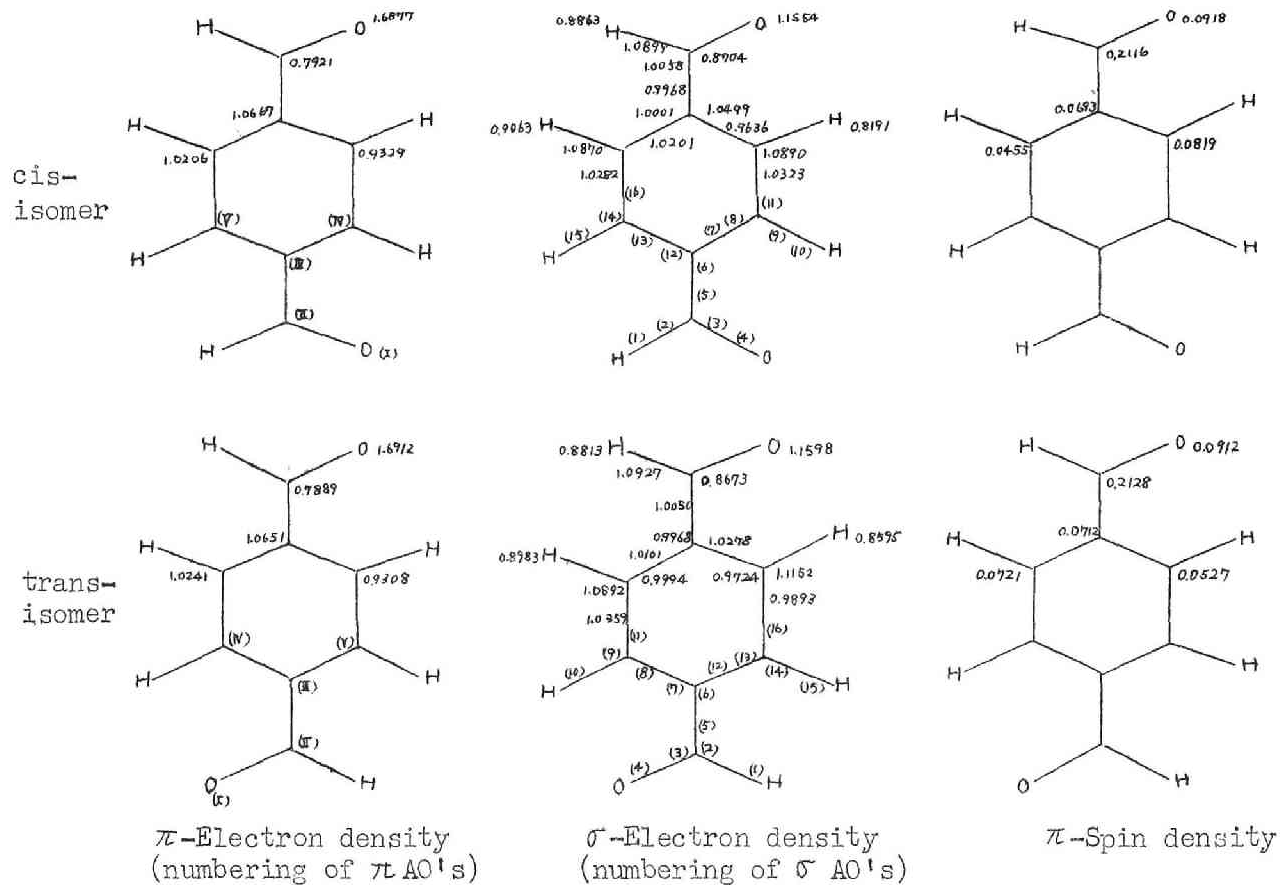


Fig. 2 Electron densities of the first order of the aldehyde anion radical isomers (numbering of AO's in parentheses)

Table I Values of a_{AB} for Various Pairs of Atoms

$\begin{array}{c} A \\ \diagdown \\ B \end{array}$	C	H	O
C	1.29	1.20	1.14
H	1.20	1.12	1.05
O	1.14	1.05	0.99

Table II Values of Parameters a_{rr}° , a_{rs}° , b_{tt}° and b_{tu}° of the Zero Order*

a_{rr}° : Coulomb Integral of π AO's		a_{rs}° : Resonance Integral between π AO's	
O	2	C _{II} -O	1.4
C _{II}	0.2	C-C	1
C(others)	0		
b_{tt}° : Coulomb Integral of σ AO's		b_{tu}° : Resonance Integral between σ AO's	
O	0.3	C-O	1.1
C	0	C-H	0.94
H	-0.2	C-C(bonding)	1
		C-C(on the same atom)	0.38

* As to the numbering AO's, see Fig. 1.

Table III Values of Parameters a_{rr}^1 and b_{tt}^1 of the First Order*

cis		trans	
a_{rr}^1 : Coulomb Integral of π AO's		a_{rr}^1 : Coulomb Integral of π AO's	
O_I	1.976	O_I	2.0(standard)
C_{II}	0.2(invariant)	C_{II}	0.2(invariant)
C_{III}	0 (invariant)	C_{III}	0 (invariant)
C_{IV}	-0.230	C_{IV}	-0.146
C_V	0.084	C_V	0 (standard)
b_{tt}^1 : Coulomb Integral of σ AO's		b_{tt}^1 : Coulomb Integral of σ AO's	
H_1	-0.193	H_1	-0.2(standard)
C_2, C_3, C_5	0 (invariant)	C_2, C_3, C_5	0 (invariant)
O_4	+0.292	O_4	+0.3(standard)
C_6, C_7, C_{12}	0 (invariant)	C_6, C_7, C_{12}	0 (invariant)
C_8, C_9, C_{11}	-0.072	C_8, C_9, C_{11}	-0.046
H_{10}	-0.336	H_{10}	-0.299
C_{13}, C_{14}, C_{16}	+0.026	C_{13}, C_{14}, C_{16}	0 (standard)
H_{15}	-0.164	H_{15}	-0.2(standard)

* As to numbering of AO's, see Fig. 2

Table IV Calculated and Experimental Spin Densities
and Assignment of Coupling Constants of
Terephthalaldehyde Anion

Calculated(cis isomer)		Experimental (species A)
Position	Spin density	Spin density
C _I	0.212	0.169
C _W	0.082	0.090
C _V	0.046	0.030
Calculated(trans isomer)		Experimental(species B)
Position	Spin density	Spin density
C _I	0.213	0.166
C _W	0.053	0.050
C _V	0.072	0.067

Table V Electron Density of Each Occupied π MO

1. cis Isomer

Orbital Energy λ_i	Symmetry**	Electron Density	
		on C _{IV}	on C _V
-0.1498*	A'	0.0819	0.0455
+0.9204	A'	0.2662	0.2253
+1.1815	A''	0.0493	0.0652
+1.9686	A'	0.1001	0.1838
+2.8555	A''	0.0015	0.0017
+2.8876	A'	0.0085	0.0117

* Half Occupied Level

** Symmetry in C_{1h} Group

2. trans Isomer

Orbital Energy λ_i	Symmetry**	Electron Density	
		on C _{IV}	on C _V
-0.1383*	A	0.0527	0.0721
+0.9240	B	0.2661	0.2255
+1.1872	B	0.0291	0.0922
+1.9597	A	0.1334	0.1469
+2.8716	B	0.0014	0.0016
+2.9021	A	0.0090	0.0097

* Half Occupied Level

** Symmetry in C₂ Group

Chapter 8

Angular Dependency of ESR Proton Hyperfine

Coupling Constant of CH₂ Group

§1. Introduction

Recent ESR studies on organic radicals in the solid state have revealed several interesting facts on the structures of these radicals. It would be one of these facts that in some radicals β protons--protons in methyl or methylene groups adjacent to the carbon atom which brings an odd electron--are chemically distinct from each other.

Heller and McConnell¹⁾ studied the ESR spectra of γ irradiated single crystal of succinic acid and analyzed them to show that the radical produced was identified as shown in Fig. 1a and the coupling constants (nearly isotropic) of the two protons, H₁ and H₂, were not equal. They concluded that the distinction was caused by a kind of deformation of CH₂ group: the H-C-H angle was no longer bisected by the molecular plane. They assumed the following equation for the angular dependency of the coupling constant of β -protons:

$$a_H(\theta) = \rho_\alpha^\circ K \cos^2 \theta \quad (1)$$

In the equation $a_H(\theta)$ is the isotropic hyperfine coupling constant of β protons, ρ_α° is the spin density on the carbon (α carbon) adjacent to the methylene group, θ is the angle between the carbon $p\pi$ orbital on the α carbon and each of the C-H bonds both projected to a plane perpendicular to the $C_\alpha - C_\beta$ bond, as shown in Fig. 2. In this expression they seem to have assumed that the type of the deformation would be the rotation of the alkyl group around the $C_\alpha - C_\beta$ axis.

After that Kurita and Gordy²⁾ found a similar distinction between the two protons in a CH_2 group on studying the ESR of the γ irradiated single crystal of L-glycine hydrochloride. In this case the radical was identified as that shown in Fig. 1b and the coupling constants were $a_{H1} = 9 \text{ gauss}$ and $a_{H2} = 2 \text{ gauss}$. If we simply applied Eq. 1 to the discussion of the ratio a_{H1}/a_{H2} , the deformation would have to be very large. Pooley and Whiffen³⁾ also observed different coupling constants of β protons in the radical $HOOCCH_2CHCOOH$ from succinic acid (100 Mc and 80 Mc). Jasejã and Anderson⁴⁾ obtained a different pair of unequal coupling constants (115 Mc and 18 Mc) in the same radical $HOOCCH_2CHCOOH$ from aspartic acid, attributing the cause of deformation to intermolecular forces. In both of the papers

the deformation angle was discussed by the $\cos^2 \theta$ rule.

Recently Ohnishi, Sugimoto and Nitta⁵⁾ have carefully studied the temperature dependency of the ESR spectra of the radical in γ irradiated stretched polyethylene which had been assigned to the allyl type radical shown in Fig. 1c, and have found that at low temperature (-180°C) the protons in CH_2 groups adjacent to the allyl group, H_1 and H_2 in the figure, give different isotropic hyperfine coupling constants, that is, 30 and 11 gauss, respectively, and at high temperature ($+142^\circ\text{C}$) the distinction disappears and the both constants come to 21.3 gauss. Adopting Eq. 1 the calculated θ of H_1 and H_2 are obtained $55^\circ 02'$ and $18^\circ 52'$. The deviation from the normal angle, 30° , seems irrationally large.

As the mechanism of deformation the rotation would be more difficult in the case of methylene group, CH_2R , than in the case of methyl group, $-\text{CH}_3$ because of the bulky group $-\text{COOH}$, alkyl and so forth, attached to the former. Especially in polymeric solids like stretched polyethylene the group R being a very long chain, the rotation around $\text{C}_\alpha - \text{C}_\beta$ axis would be almost hindered. In this case the deformation would be performed by rocking, twisting, or others.

In the present paper we considered two typical mechanisms of deformation: one is the rotation around the $\text{C}_\alpha - \text{C}_\beta$

axis and the other is the rocking of CH_2 group in a plane on which normally the two C-H bonds of the CH_2 group exist, and made a valence bond calculation on the spin density on CH_2 protons for their various conformations caused by the rotation and the rocking, in order to see what angular dependency proton hyperfine coupling constants on CH_2 groups obey.

The fact that we assumed rotation and rocking as a source of non-equivalent coupling constants does not necessarily mean that the energy minimum is accomplished by these kinds of deformation. A possibility that one hydrogen is attracted to the odd p orbital making a bent bond might be considered as well as a possibility of twisting. It would be very interesting to study theoretically what is the most stable conformation and why such a deformed conformation could be stable, but calculation seems to be awfully complicated in order to explain such slight difference in conformational energy and hence this problem would not be discussed in this chapter.

§2. Method of Calculation

In calculating the ground state wave function and the spin density in the state is employed the hypothetical system

consisting of 5 valence electrons on the five atomic orbitals as shown in Fig. 3: the $2p\pi$ orbital (designated by P) on the carbon in which an odd electron is situated, the two hybridized orbitals (σ_1 and σ_2) on the carbon β and the two $1s$ orbitals (H_1 and H_2) on the two hydrogens which are bonding with the hybridized orbitals σ_1 and σ_2 , respectively. In their normal conformation $C_\alpha C_\beta C_\gamma$ chain is situated on the plane U and the two CH bonds are on the plane V which is perpendicular to the plane U and bisecting the $C_\alpha C_\beta C_\gamma$ angle.

All canonical structures that have maximum bondings, that is, five structures are taken as the bases of the valence bond calculation, but all ionic structures were neglected. This neglect would result in a larger spin density on hydrogen atoms; but we are going to discuss the relative change of the spin distribution by the variation of conformation because of the uncertainty involved in evaluating atomic integrals that will be mentioned later, and so far the neglect would not affect the conclusion.

Throughout the calculation the deformation is considered to cause the corresponding change in the hybridization of the carbon orbitals making the deformed bonds and the hydrogen atoms are always regarded to be in the direction of the

hybridized orbitals with the CH bond length which is not changed by the deformation.

In treating rotating conformations the four hybridized orbitals, σ_1 , σ_2 , σ_3 and σ_4 remain sp^3 hybridized. The calculation of the spin density was made for various rotated angles around the $C_\alpha - C_\beta$ axis.

In treating rocking conformation, the hybridized orbitals on the carbon β are written with the two parameters a and b . Parameter a corresponds to the variation of the $C_\alpha C_\beta C_\gamma$ angle. It is the reason why we considered this kind of deformation that, for instance, as to the allyl type radical in oriented polyethylene mentioned above the polyethylene main chain would be fixed and in order to decrease the strain the allyl radical might change the angle φ of $C_\alpha C_\beta C_\gamma$. In our calculation the angle φ is expressed in terms of the parameter a which designates the hybridization of the orbitals σ_3 and σ_4 : a^2 is the s nature of the orbitals σ_3 and σ_4 , as can be seen in the followings.

$$\varphi = \cos^{-1}\{a^2/(a^2 - 1)\} \quad (2)$$

$$\left. \begin{aligned} \sigma_3 &= a\psi_{\beta 2s} - \sqrt{(1-2a^2)/2} \psi_{\beta 2px} + (1/\sqrt{2})\psi_{\beta 2py} \\ \sigma_4 &= a\psi_{\beta 2s} - \sqrt{(1-2a^2)/2} \psi_{\beta 2px} - (1/\sqrt{2})\psi_{\beta 2py} \end{aligned} \right\} \quad (3)$$

where $\psi_{\beta 2s}$, $\psi_{\beta 2px}$ and $\psi_{\beta 2py}$ are 2s, 2px and 2py orbitals on the β carbon, respectively, the coordinates being taken as shown in Fig. 3.

In any conformation with varied a value and with various magnitude of rocking of the two CH bonds, it is assumed that the $C_{\alpha}C_{\beta}C_{\gamma}$ chain and, consequently, the orbitals σ_3 and σ_4 are always in the plane U which is perpendicular to the odd p orbital P, and that the orbitals σ_1 , σ_2 , H_1 and H_2 are in the plane V parallel to P and bisecting the angle φ . The other parameter b is utilized to stand for the hybridization of the orbital σ_1 : b^2 being the s nature of the orbital σ_1 , the s nature of the orbital σ_2 is $1-2a^2-b^2$. Exact form of the orbitals σ_1 and σ_2 is written as follows.

$$\left. \begin{aligned} \sigma_1 &= b\psi_{\beta 2s} + (\sqrt{2}ab/\sqrt{1-2a^2})\psi_{\beta 2px} + (\sqrt{1-2a^2-b^2}/\sqrt{1-2a^2})\psi_{\beta 2pz} \\ \sigma_2 &= \sqrt{1-2a^2-b^2}\psi_{\beta 2s} + (\sqrt{2}a\sqrt{1-2a^2-b^2}/\sqrt{1-2a^2})\psi_{\beta 2px} - (b/\sqrt{1-2a^2})\psi_{\beta 2pz} \end{aligned} \right\} (4)$$

Calculation is carried out for the following three values of a
 Series 1: $a = \frac{1}{2}$, i.e., σ_3 and σ_4 are both sp^3 hybridized (s nature 25%) and consequently the $C_{\alpha}C_{\beta}C_{\gamma}$ angle is $109^{\circ}28'$ (normal). Hybridization of σ_1 is varied from sp^3 to p, at the same time that of σ_2 from sp^3 to sp.

Series 2: $a = 1/\sqrt{5}$: σ_3 and σ_4 are both sp^4 hybridized (s nature 20%) and consequently the $C_{\alpha}C_{\beta}C_{\gamma}$ angle is $104^{\circ}29'$, narrower than normal.

Series 3: $\alpha = \sqrt{3/10}$: σ_3 and σ_4 are both s^3p^7 hybridized (s nature 30%) and the $C\alpha C_\beta C_\gamma$ angle is $114^\circ 23'$, obtuser than normal.

The angles θ_1 and θ_2 defined in Fig. 2 are easily connected with the parameters a and b , as follows:

$$\left. \begin{aligned} \tan \theta_1 &= ab / \sqrt{1-2a^2-b^2} \sqrt{1-a^2} \\ \tan \theta_2 &= a \sqrt{1-2a^2-b^2} / b \sqrt{1-a^2} \end{aligned} \right\} \quad (5)$$

And the following relationship between the angle θ_1 and θ_2 , as a function of the parameter a but independent of the parameter b , would be used in the following section in checking the calculated results.

$$\tan \theta_1 \tan \theta_2 = a^2 / (1 - a^2) \quad (6)$$

Matrix elements between canonical structures are reduced to those between hybridized orbitals by the usual method; and those are also reduced to those between atomic orbitals by Eqs. 3 and 4.

Atomic exchange integrals requisite to the calculation are evaluated according to the method by van Vleck⁽⁶⁾ and by Karplus et al.⁽⁷⁾ The values of integrals employed are collected in Table I. Nrs's in the table are the following exchange integrals between $C\beta$ and H_1 or H_2

$$N_{rs} = - \int \psi_{\beta r}(1) \psi_{H1s}(2) \cdots H \psi_{H1s}(1) \psi_{\beta s}(2) \cdots d\tau \quad (7)$$

H: total hamiltonian

and are evaluated from the dissociation energy of methane and the heat of sublimation of graphite. All N_{rs} 's between C_{α} and H_i are neglected because they are small. F_0 's and F_2 and G_i are the usual one-center atomic integrals of C_{β} , whose values are deduced from spectroscopic data of a carbon atom. Exchange integral $[H_1, H_2]$ between H_1 and H_2 is calculated on the Morse function as a function of their interatomic distance. There seems no reliable method available for evaluating exchange integrals N_{rstu} between C_{α} and C_{β} .

$$N_{rstu} = \int \psi_{\alpha r}(1) \psi_{\beta s}(2) \cdots H \psi_{\beta t}(1) \psi_{\alpha u}(2) \cdots d\tau \quad (8)$$

In this chapter, except for $N_{\pi\pi\pi\pi}$, the effective two electron hamiltonian approximation by Karplus⁷⁾ is used, giving the following results:

$$N_{rstu} = \int \psi_{\alpha r}(1) \psi_{\beta s}(2) \frac{e^2}{r_{12}} \psi_{\beta t}(1) \psi_{\alpha u}(2) d\tau_1 d\tau_2 \quad (9)$$

$$\left(\begin{array}{l} \text{for } (r,u) = (2p\pi, 2p\pi) \\ s,t = 2s, 2p\sigma, 2p\pi' \end{array} \right)$$

As to $N_{\pi\pi\pi\pi}$, Altman's result⁸⁾ is adopted.

The overlap integrals between atomic orbitals are entirely neglected in order to simplify the calculation.

§3. Result and Discussion

Calculated spin densities on protons for rotating conformations of various angles are tabulated in Table II, together with spin densities on β carbon hybridized orbitals. From the spin density, ρ_H , on the proton one can calculate the coupling constant a_H by the following equation:

$$a_H = Q \rho_H \quad (10)$$

Q being the coupling constant of proton when ρ_H is unity. In the normal conformation both θ_1 and θ_2 are 30° . Spin density on a proton does not seem to be dependent only on its own projection angle, say θ_1 , but also on the angle of the other proton, say θ_2 , which one can see by comparing Calc. Nos.1 and 4 where ρ_H is different for the same θ , 30° . The situation is the same in Calc. Nos.3 and 5. Roughly speaking, however, it varies in accord with $\cos^2 \theta$ as one might see in Fig. 4. In Fig. 4 the curve $\rho_H = \text{const} \times \cos^2 \theta$ is drawn so as to fit the calculated result (Calc. No.1) at $\theta = 30^\circ$. Accordingly, it may be said that the $\cos^2 \theta$ rule may be utilized for the hyperfine coupling of CH_2 protons

in the rotating conformation.

Spin density on the hybridized orbitals increases with the increased spin density on the proton of the CH bond, as is seen in Table II. Thus as the isotropic coupling constant of the methylenic proton (deformed by rotation) becomes large, the anisotropy of the coupling will get large, though the magnitude of anisotropy seems to be negligibly small.

Results of calculation for rocking conformations are collected in Tables III, IV and V, together with spin densities on β carbon hybridized orbitals and the s nature of the latter. The angular dependency of proton spin densities in the case of rocking conformations is entirely different from that in the case of rotating conformations, as is illustrated in Fig. 5. It should be stressed that the $\cos^2\theta$ rule applies by no means to the proton coupling of methylene group in the rocking conformation: the proton coupling constant varies more rapidly with the projection angle θ . If one tries to use the $\cos^2\theta$ rule to the rocking methylene group, one will be led to a larger deformation from the normal sites than it is. Actually the rotation and the rocking and other kinds of deformation would take place in the methylene group which gives unequal proton coupling constants for the two protons, and therefore minute care should be paid in discussing the deformation angle of methylene group in the

basis of its proton coupling constants.

Proton spin density in the case of this deformation is not simply a function of θ . For instance, negative spin density on the proton nearly in the plane U (for example, -0.0459 in Calc. No. 7 in Table III) does not seem to be originated from the direct interaction of the CH bond with the odd orbital P, but from the mixing of the interaction of the CH bond with the other CH bond and of the interaction of the latter with the orbital P. This is shown by a valence bond calculation on the system consisting of the three atomic orbitals (P, and σ and H orbitals of the bond in the plane U) : proton spin density in this case is calculated to be -0.0036, which is ten times smaller in magnitude than the spin density shown above.

There may occur actually other kinds of deformation than rotation and rocking. So far as the spin density is concerned, other deformations, for instance twisting, might be derived as a mixing of rotation and rocking in the first approximation.

The effect of the $C_\alpha C_\beta C_\gamma$ angle, φ , to the proton spin density will be seen in comparing Table III with Tables IV and V, or in Fig. 5. Generally speaking, the larger φ value results in the larger (in absolute value) proton

spin density for the same hybridization or the same b value, though the difference is relatively small. For a minute discussion this difference should be taken into consideration. But for a rough estimation of the rocking angle the calculated spin density and its interpolation for the normal φ value (Table III) would be safely used.

Spin density on β carbon hybridized orbitals varies almost parallel with that on the proton in the bond, which also can be seen in Tables III, IV and V. Thus the anisotropy of the proton coupling constant would become important for protons whose projection angle is smaller than 20° .

§4. Application to Allyl Type Radical in Oriented Polyethylene

We would like to apply the result of the preceding section to the coupling constants of the two non-equivalent protons in methylene group adjacent to allyl type radical in oriented polyethylene, which were observed by Ohnishi et al.⁵⁾ Application to this problem would be appropriate and rational because, as was mentioned previously, the allyl radical, which is produced in a midway of an oriented polyethylene molecule, would not be able to rotate because of the

long main chain of the molecule, but it would be able to rock, because rocking need not any motion of main obtain.

Observed coupling constants by them are given in Table VI, where -180°C is the temperature at which the deformation of methylene group seems to be entirely frozen to the minima of the potential energy (probably double minima on either side of the normal conformation) and $+142^{\circ}\text{C}$ is the one at which the transformation from one minimum to the other is perfectly free.

At first for comparison's sake the $\cos^2\theta$ rule is employed to estimate the projection angle. If 21.3 gauss at $+142^{\circ}\text{C}$ is assumed to correspond to $\theta = 30^{\circ}$, 30 gauss at -182°C cannot be achieved by any θ value (Table VI). On the other hand, if empirically deduced $K = 58$ gauss and SCF π spin density on α carbon of allyl radical $\rho_{\alpha}^{\pi} = 0.622$ is used to Eq. 1, an unexpectedly large deformation from normal angle (30°) is obtained (Table VI).

In our valence bond calculation an odd electron on π carbon orbital (P) interacting with β CH bonds are treated. But in allyl radical which is a conjugated system the number of odd electron on P is not unity but ρ_{α}^{π} . So, instead of Eq. 10, Eq. 11 may be used in the first approximation.

$$a_H = \rho_\alpha^\circ \rho_H Q \quad (11)$$

Q is theoretically given to be 507 gauss and $\rho_\alpha^\circ = 0.622$ as stated above and a_H is observed, and then ρ_H can be calculated and consequently the angle θ will be deduced. But as the numerical value of the calculated proton spin density ρ_H may include some error caused by the approximations employed, e.g., neglect of overlap integrals and neglect of ionic structures, it seems more rational to take ρ_H as compared in its relative value. That is to say, regarding the product $\rho_\alpha^\circ Q$ as a parameter to be decided experimentally, we connect the observed a_H to ρ_H and θ , and use one more relation, Eq. 6, to check the consistency of the assignment.

First we assume the radical has the conformation where $a = 0.250$, that is, $\varphi = 109^\circ 28'$. Then the coupling 21.3 gauss at $+142^\circ\text{C}$ will correspond to the normal site $b^2 = \frac{1}{4}$ and $\theta_1 = \theta_2 = 30^\circ 00'$, and from the calculated $\rho_H = +0.0817$ of this case $\rho_\alpha^\circ Q$ is obtained to be 261 gauss.* Using this and interpolating the calculated spin density in Series 1 (Table III), the values of θ in Table VI, $24^\circ 20'$ and $39^\circ 10'$, are obtained. This set of θ_1 and θ_2 comes to the relation

* Here if $\rho_\alpha^\circ = 0.622$ is applied, $Q = 420$ gauss is obtained. Comparing this with the theoretical value 507 gauss, is recognized some effect of neglecting ionic structures, like $\text{C}^- \text{H}^+$, which makes the calculated spin density on protons larger than it is.

$\tan \theta_1 \tan \theta_2 = 0.368$ and with the aid of Eq. 6, comes to $a^2 = 0.269$, which is larger than the assumed value $a^2 = 0.250$.

Secondly, if the conformation of the radical is assumed to be the case $a^2 = 0.333$, i.e., $\varphi = 114^\circ 23'$, are obtained the results in the last line of Table VI and $a^2 = 0.317$, which is smaller than the assumed one.

Thus the value of a^2 in the allyl radical obtained between $\frac{1}{4}$ and $1/3$, and therefore φ lies between $109^\circ 28'$ and $114^\circ 23'$: widening of the $C_\alpha C_\beta C_\gamma$ angle from the tetrahedral angle seems to take place in this allyl type radical. The deformation from the equivalent sites derived by our rocking model is 6° to 9° , which is much smaller and more probable than 18° or more by the $\cos^2 \theta$ rule.

By considering the difference of the bond length between the CC single bond and the allyl CC bond, widening of the $C_\alpha C_\beta C_\gamma$ angle is proved to be probable for the radical to reduce the strain.⁵⁾

In the present chapter we applied our calculation based on the rocking conformations only to the allyl type radical in polyethylene, but unequal couplings of some organic radicals in single crystals and in rigid glass also seem to have to be partly reexamined by this result.

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Fig. 1a

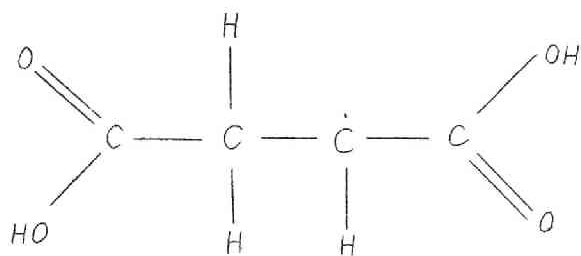


Fig. 1b

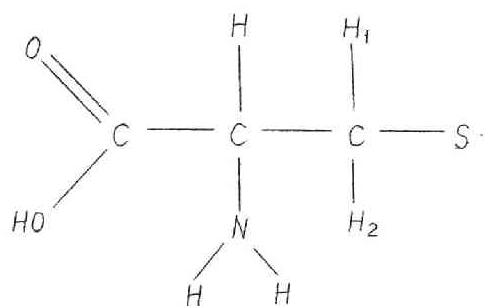
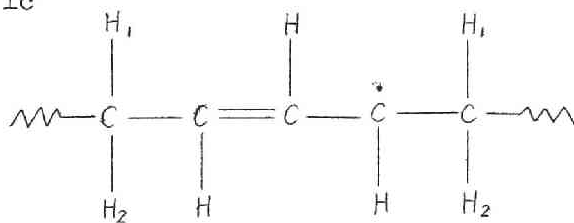
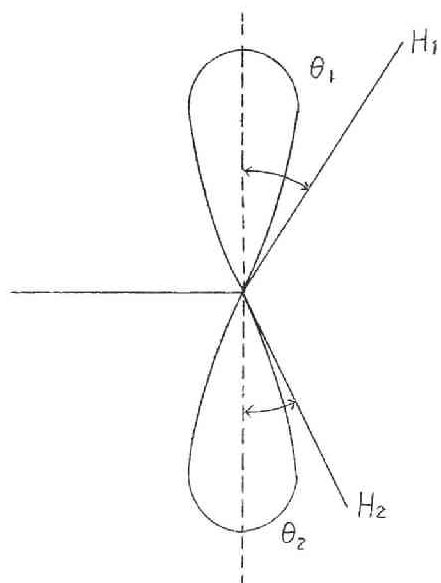
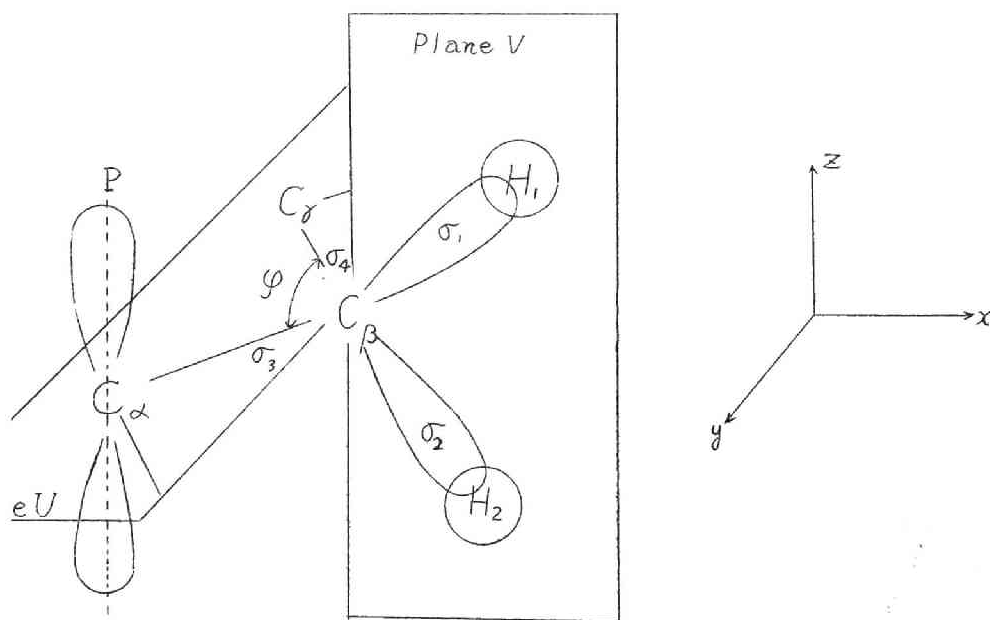


Fig. 1c





ig. 2 Projection angles θ_1 and θ_2



3 The model of calculation and the notation used

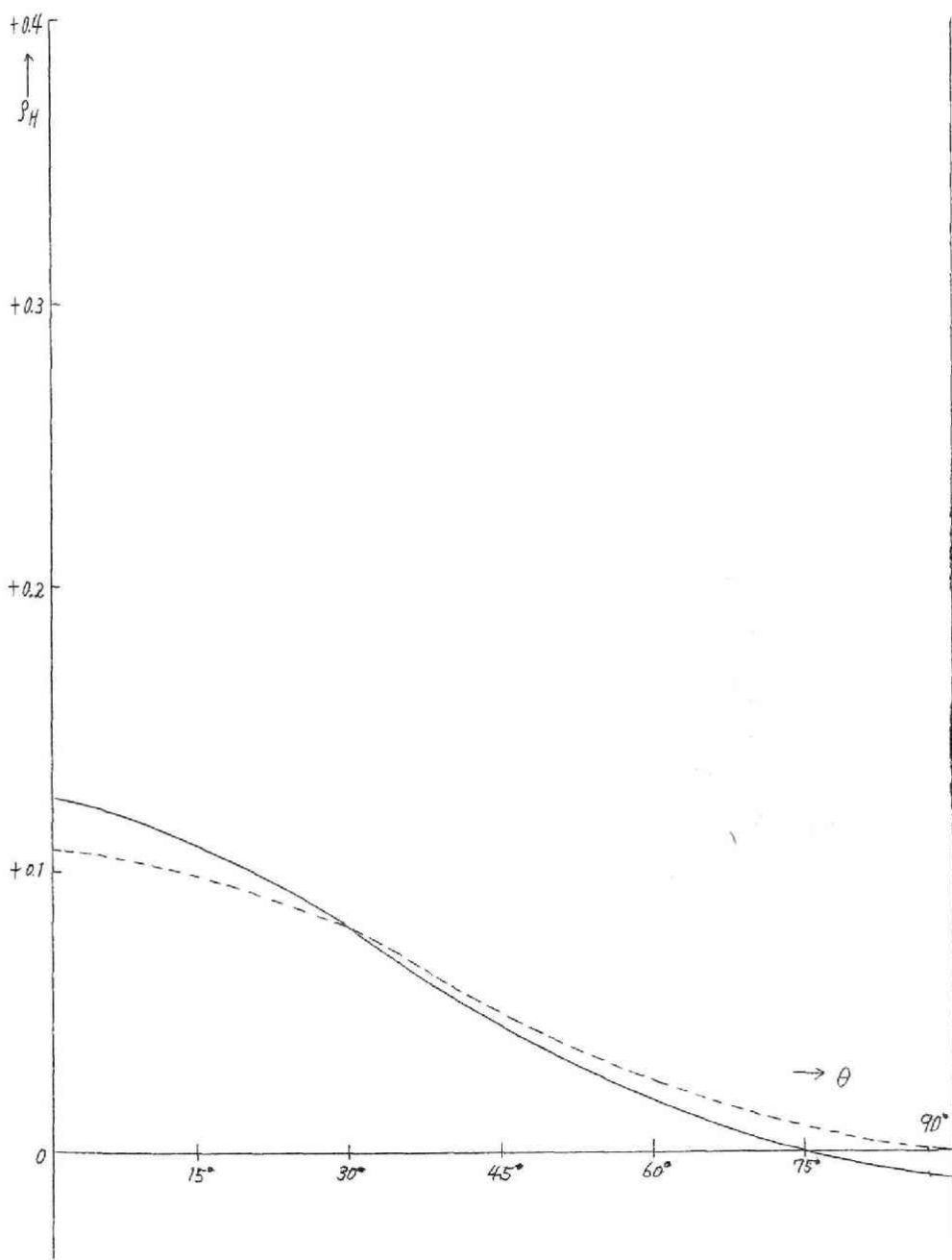


Fig. 4 Angular dependency of proton spin density
for rotation —:calculated; ---:const $\times \cos^2 \theta$

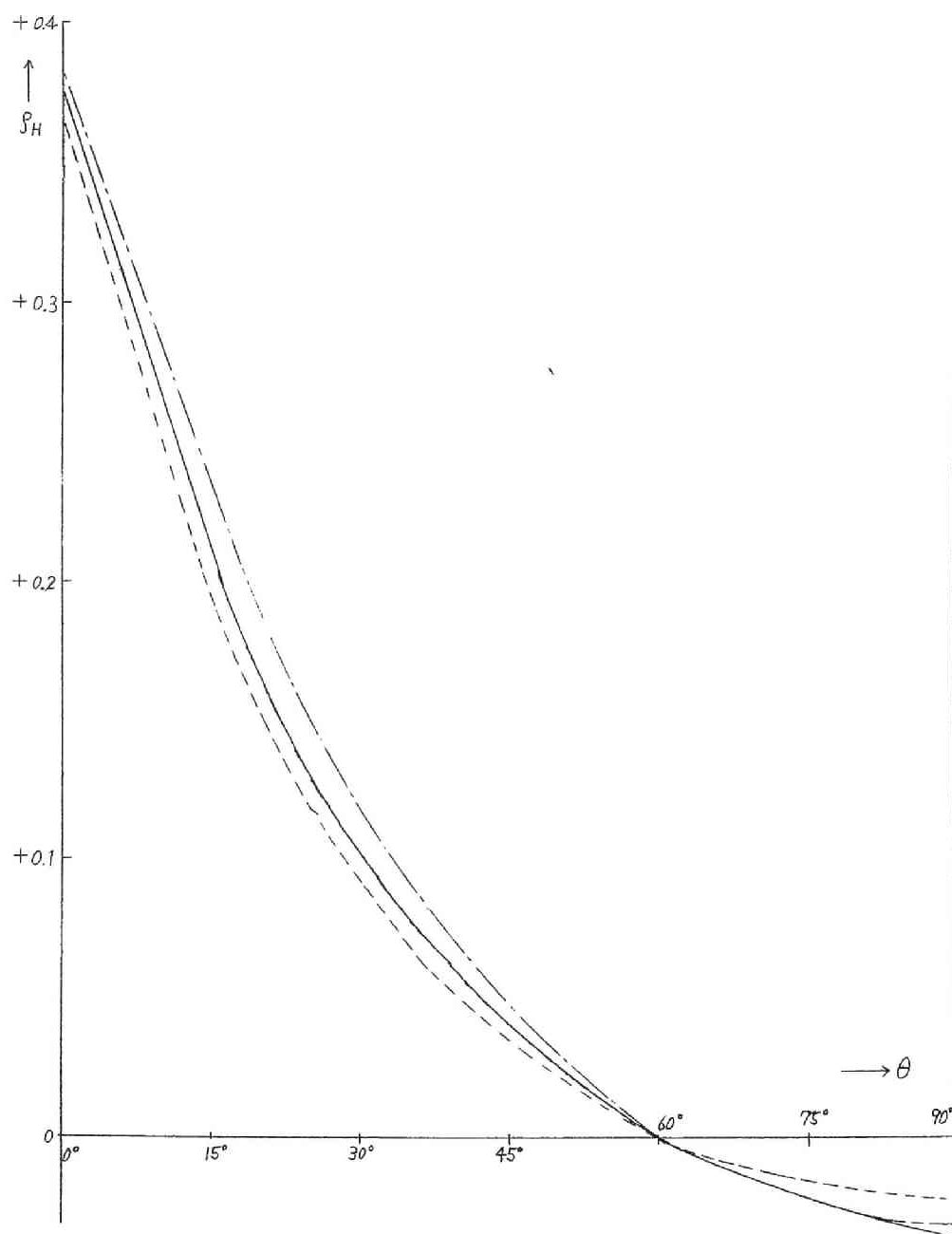


Fig. 5 Angular dependency of proton spin density for rocking. —: series 1; --- series 2; —·—·— series 3

Table I Values of Exchange Integrals Employed

(In Units of eV)

Exchange integrals between C_β and H

N_{ss}	2.00
$N_{s\sigma}$	1.82
$N_{\sigma\sigma}$	2.30
$N_{\pi\pi}$	-0.60

Exchange integrals in C_β

$F_0(2s, 2s) - 2F_0(2s, 2p) + F_0(2p, 2p)$	0.430
F_2	0.231
G_1	2.415

Exchange integrals between H_1 and H_2

[H_1, H_2] Morse function

Exchange integrals between C_β and P

$N_{\pi ss\pi}$	0.207
$N_{\pi\sigma s\pi}$	-0.253
$N_{\pi\sigma\sigma\pi}$	0.348
$N_{\pi\pi\pi\pi}$	-1.240
$N_{\pi\pi'\pi\pi}$	0.026

Table II Calculated Spin Density for Various Rotating Conformations

Calc. No.	Rotation from Normal Site	Projection Angle		Proton Spin Density		β Carbon Spin Density	
		θ_1	θ_2	ρ_{H_1}	ρ_{H_2}	ρ_{C_1}	ρ_{C_2}
1	0°	30°	30°	+0.0817	+0.0817	-0.0753	-0.0753
2	10°	20°	40°	+ .1039	+ .0565	- .0941	- .0530
3	30°	0°	60°	+ .1262	+ .0108	- .1124	- .0098
4	60°	30°	90°	+ .0734	- .0108	- .0687	+ .0113
5	90°	60°	60°	+ .0233	+ .0233	- .0228	- .0228

Table III Calculated Spin Density for Various Rocking Conformations

(Series 1 : $a^2 = 1/4$, $\varphi = 109^\circ 28'$)

Calc. No.	Parameter b	Nature of Hybridized Orbital		Projection Angle		Proton Spin Density		β Carbon Spin Density	
		σ_1	σ_2	θ_1	θ_2	ρ_{H1}	ρ_{H2}	ρ_{σ_1}	ρ_{σ_2}
1	1/2	0.250	0.250	$30^\circ 00'$	$30^\circ 00'$	+0.0817	+0.0817	-0.0753	-0.0753
2	$1/\sqrt{5}$.200	.300	$25^\circ 14'$	$35^\circ 16'$	+ .1097	+ .0567	- .0988	- .0531
3	$1/\sqrt{6}$.167	.333	$22^\circ 13'$	$39^\circ 14'$	+ .1273	+ .0422	- .1129	- .0399
4	1/3	.111	.389	$17^\circ 09'$	$47^\circ 12'$	+ .1719	+ .0178	- .1465	- .0167
5	$1/\sqrt{14}$.071	.429	$13^\circ 16'$	$54^\circ 44'$	+ .2094	+ .0017	- .1723	- .0009
6	1/5	.040	.460	$9^\circ 40'$	$62^\circ 57'$	+ .2491	- .0119	- .1975	+ .0129
7	0	0	.500	0°	$90^\circ 00'$	+ .3829	- .0459	- .2662	+ .0497

Table IV Calculated Spin Density for Various Rocking Conformations

(Series 2 : $a^2 = 1/5$, $\varphi = 104^\circ 29'$)

Calc. No.	Parameter b	Nature of Hybridized Orbital		Projection Angle		Proton Spin Density		β Carbon Spin Density	
		σ_1	σ_2	θ_1	θ_2	ρ_{H_1}	ρ_{H_2}	ρ_{σ_1}	ρ_{σ_2}
1	$\sqrt{3/10}$	0.333	0.333	$26^\circ 34'$	$26^\circ 34'$	+0.0816	+0.0816	-0.0752	-0.0752
2	$1/2$.250	.350	$22^\circ 54'$	$30^\circ 37'$	+ .1035	+ .0626	- .0936	- .0586
3	$1/\sqrt{5}$.200	.400	$19^\circ 28'$	$35^\circ 16'$	+ .1280	+ .0453	- .1133	- .0430
4	$1/\sqrt{6}$.167	.433	$17^\circ 14'$	$38^\circ 55'$	+ .1455	+ .0348	- .1268	- .0333
5	$1/3$.111	.489	$13^\circ 24'$	$46^\circ 22'$	+ .1827	+ .0182	- .1538	- .0177
6	$1/\sqrt{15}$.067	.533	$10^\circ 01'$	$54^\circ 44'$	+ .2207	+ .0058	- .1792	- .0058
7	$1/5$.040	.560	$7^\circ 37'$	$61^\circ 52'$	+ .2529	- .0048	- .1991	+ .0049
8	0	0	.600	0°	$90^\circ 00'$	+ .3786	- .0277	- .2631	+ .0280

Table V Calculated Spin Density for Various Rocking Conformations
(Series 3 : $a^2 = 3/10$, $\varphi = 114^\circ 23'$)

Calc. No.	Parameter b	Nature of Hybridized Orbital		Projection Angle		Proton Spin Density		β Carbon Spin Density	
		σ_1	σ_2	θ_1	θ_2	ρ_{H_1}	ρ_{H_2}	ρ_{σ_1}	ρ_{σ_2}
1	$1/\sqrt{5}$	0.200	0.200	$33^\circ 13'$	$33^\circ 13'$	+0.0819	+0.0819	-0.0753	-0.0753
2	$1/\sqrt{6}$.167	.233	$28^\circ 57'$	$37^\circ 46'$	+ .1063	+ .0584	- .0960	- .0544
3	$1/3$.111	.289	$22^\circ 06'$	$46^\circ 35'$	+ .1541	+ .0219	- .1339	- .0199
4	$1/\sqrt{15}$.067	.333	$16^\circ 19'$	$55^\circ 40'$	+ .2040	- .0031	- .1694	+ .0050
5	$1/5$.040	.360	$12^\circ 18'$	$63^\circ 01'$	+ .2433	- .0197	- .1946	+ .0222
6	0	0	.400	0°	$90^\circ 00'$	+ .3858	- .0371	- .2679	+ .0403

Table VI Observed Hyperfine Coupling Constant and Estimated Projection Angle θ
by Several Methods

		H_1	H_2	H_1 and H_2
		$(-180^\circ\text{C})*$	$(-180^\circ\text{C})*$	$(+142^\circ\text{C})*$
Observed coupling constant ⁵⁾		30 gauss	11 gauss	21.3 gauss
Projection angle θ	$\cos^2 \theta$ rule (21.3 gauss is assigned to $30^\circ 00'$)	impossible	$51^\circ 32'$	$30^\circ 00'$ (assumed)
	$\cos^2 \theta$ rule ($K=58$ gauss)	$18^\circ 52'$	$55^\circ 02'$	$37^\circ 06'$
	Rocking Deformation ($a^2 = 1/4$)	$24^\circ 20'$	$39^\circ 10'$	$30^\circ 00'$
	Rocking Deformation ($a^2 = 1/3$)	$27^\circ 30'$	$41^\circ 49'$	$33^\circ 13'$

* Observation temperature

Chapter 9

Theoretical Assignment of ESR Spectra of Cyclohexadienyl $C_6H_7\cdot$ and Phenyl $C_6H_5\cdot$ Radicals

§1. Introduction

Assignment of observed unknown spectra to a certain radical is often liable to involve some ambiguities. One example is seen in radicals from benzene and substituted benzenes.

Fischer¹⁾ irradiated benzene, toluene, ethylbenzene, cumene, fluorobenzene and chlorobenzene with electron beam at 77°K and observed the same spectrum from all of the studied compounds, which consists of a main triplet of the splitting of 50 ± 2 gauss, each component of which separates into four triplets with the splittings 10.6 ± 0.5 gauss (quartet) and 2.6 ± 0.2 gauss (triplet). He ascribed the spectrum to cyclohexadienyl radical, $C_6H_7\cdot$, with the largest splitting 50 gauss of the two methylene protons, with the splitting 10.6 gauss of the two ortho and the one para protons and with the smallest splitting 2.6 gauss of the two meta protons.

Ohnishi et al.²⁾ studied ESR spectra of radicals produced by electron beam irradiation at 77°K on benzene, toluene, chlorobenzene, phenylcyclohexane, benzoic acid and

xylenes. For benzene at the observation temperature lower than -50°C they obtained a triplet spectrum with a quartet structure, each component having a finer triplet structure with the splittings 47.5 gauss (triplet), 10.4 gauss (quartet) and 2.5 gauss (triplet), respectively. At the higher temperature this spectrum disappeared and there remained another singlet spectrum with the width ΔH_{msl} of 25 gauss. The former complex spectrum which is very close to that by Fischer was attributed to cyclohexadienyl radical as well as Fischer, while the latter singlet spectrum was ascribed to phenyl radical $\text{C}_6\text{H}_5\cdot$. Kuwata³⁾ observed a broad spectrum from UV irradiated halogenobenzenes, which was considered to originate from phenyl radical.

On the other hand, ЧХЕНДЗЕ et al.⁴⁾ irradiated benzene with electron beam and observed a triplet spectrum with the intensity ratio 1:2:1 and the splitting 45.0 ± 1.5 gauss, whose each component separates into a quartet with the splitting 10.2 ± 0.5 gauss. Though the spectrum seems to resemble very closely those by Fischer and by Ohnishi et al., according to ЧХЕНДЗЕ et al. it was the spectrum of phenyl radical where the largest triplet was assigned to the two ortho protons and the quartet to the two meta and the one para protons.

As we explained here, the assignment of the two kinds of observed spectra, the triplet with quartet structures and the broad singlet, is still a matter to be settled. Judging from the historical evidence that theoretical calculations and discussions have offered many foundations on interpretation of ESR spectra, it seems to be worth while to make a valence bond calculation on cyclohexadienyl and phenyl radicals and to compute spin densities or the coupling constants of protons, which will be given in the present chapter.

§2. Valence Bond Calculation of Proton

Coupling Constants in Cyclohexadienyl Radical

Model of $C_6H_7^{\cdot}$ Radical.-----Cyclohexadienyl radical is treated as a system consisting of 9 electrons on the following 9 atomic orbitals (Fig. 1):

o : $2p\pi$ orbital on one of the ortho carbons

o' : $2p\pi$ orbital on the other ortho carbon

m : $2p\pi$ orbital on one of the meta carbons

m' : $2p\pi$ orbital on the other meta carbon

p : $2p\pi$ orbital on the para carbon

σ : hybridized orbital on the carbon \mathcal{A} directing the

AO H

σ' : hybridized orbital on the carbon \mathcal{A} directing the

AO H'

H : hydrogen 1s orbital on the hydrogen bonding with σ
H': hydrogen 1s orbital on the other hydrogen bonding
with σ'

The plane on which the σ H and the σ' H' bonds are located is always assumed to be perpendicular to the molecular plane. As the hybridization of the methylene carbon, C β in Fig. 1, and the bond length of the C β -C $_{ortho}$ bond do not seem to have been decided experimentally, we employed the following four different sets of configurational parameters in order to see the variation of calculated results with these configurational differences.

- a) The hybridization of the carbon β in the C β -C $_{ortho}$ bonds is assumed to be sp^2 , which implies that the C-C bonds in benzene are not affected by a hydrogen addition; and therefore the hybridization of the orbitals σ and σ' is sp^5 (s nature 1/6 and p nature 5/6). The C β -C $_{ortho}$ bond length is assumed to be 1.39Å, the C-C bond length in benzene.
- b) The same hybridization as in a). The C β -C $_{ortho}$ bond length is 1.54Å, the bond length of a normal C-C single bond.
- c) The carbon β is assumed to have the tetrahedral configuration, that is, all the valence orbitals of the carbon β is sp^3 hybridized. And the C β -C $_{ortho}$ bond length is 1.39Å.
- d) The same hybridization as in c). The bond length is 1.54Å.

In all of the four sets the $C_\alpha-C_\beta-C_{\alpha'}$ angle is assumed to be 120° ; this choice of the angle hardly affects the calculation result of spin density.

Canonical Structures.-----Of all the possible canonical structures that have maximum bondings, 11 structures of lower energies corresponding Kekule and Dewar structures are taken into calculation. They are illustrated in Fig. 2.

Atomic Integrals.-----Method of evaluation of necessary atomic integrals is the same as in Part II Chapter 8⁵⁾ of this thesis, mainly the method by van Vleck⁶⁾ and by Karplus et al.⁷⁾, except for Altman's⁸⁾ exchange integrals between $p\pi$ orbitals. Employed values of the $p\pi-p\pi$ exchange integrals are $N_{\pi\pi\pi\pi}(1.39\text{\AA}) = -2.27 \text{ eV}$ and $N_{\pi\pi\pi\pi}(1.54\text{\AA}) = -1.24 \text{ eV}$. Exchange integrals between non-neighboring atomic orbitals are thoroughly neglected.

Calculation Result.-----Calculated coefficients of each canonical structures in the ground state wave function is collected in Table I, from which are derived spin densities in Fig. 3.

In Fig. 3 is also given the result of a comparative calculation on an imaginary compound in which the interaction of one of the ortho carbons with methylene group is omitted. One can clearly see that the ring formation very markedly

increases the spin density on methylene proton; the calculated spin density on the methylene protons in a ring compound is almost as twice as in an open compound.

In Fig. 3 it is obvious that the change of the hybridization of the carbon ρ does little affect the spin distribution. Thus the observed coupling constants seems to offer no information of the hybridization.

On the other hand, the change of the $C_\rho - C_{ortho}$ distance, that is, the change of the exchange integral between C_ρ and C_{ortho} influence very severely on the spin density in the methylene group. Elongation of the $C_\rho - C_{ortho}$ bond length from 1.39Å to 1.54Å reduces the methylene proton spin density by half.

From these calculated values of spin density are derived proton coupling constants in Table II, which are independent of the hybridization of C_ρ . Coupling constants of "o" protons, that is, ortho, meta and para protons are calculated by the following popular relationship between the spin density on the adjacent carbon p_π orbital, ρ_C , and the proton isotropic constants, a_H :

$$a_H = Q_{HC} \rho_C \quad (1)$$

where Q_{HC} is taken to be -22.5 gauss as usual.⁹⁾ isotropic

coupling constants of methylene protons are related to the spin densities on them by the equation:

$$a_H = Q_H \rho_H \quad (2)$$

Though a_H is theoretically given to be +507 gauss, a smaller value +420 gauss, which has been previously derived by the authors in a similar valence bond calculation on deformed methylene group,⁵⁾ would be more appropriate. It is mainly due to our approximation not considering any contribution of ionic structures. The coupling constants in Table II are calculated with the latter Q_H value.

§3. Valence Bond Calculation of Proton

Coupling Constants in Phenyl Radical

Model of C_6H_5 Radical.-----In phenyl radical migration of odd electron may be achieved in several ways. One example is such a mechanism as $\sigma - \pi$ interaction between the non-bonding σ orbital and $p\pi$ orbital both on the carbon C_1 (see Fig. 4) followed by $\pi - \pi$ migration to the $p\pi$ orbital on the ortho carbon and then by $\sigma - \pi$ interaction between the ortho $p\pi$ orbital and the ortho C-H bond. But this mechanism would be less significant because of double $\sigma - \pi$ interaction which would bring the spin density on the ortho proton of the

order 1/500.

A more probable mechanism would be direct interaction between the non-bonding σ orbital and the ortho C-H bond in the molecular plane. Therefore, in the present section we adopted the model in Fig. 4 consisting of 5 electrons on the following 5 atomic orbitals.

n : sp^2 hybridized non-bonding orbital on the carbon C_1

σ_1 : sp^2 hybridized orbital on the ortho carbon, making a C-H bond with H_1

H_1 : hydrogen 1s orbital on the hydrogen H_1

σ_2 : sp^2 hybridized orbital on the meta carbon making a C-H bond with H_2

H_2 : hydrogen 1s orbital on the hydrogen H_2

For the sake of simplicity only the C-H bonds on one side of the orbital n is considered. Inclusion of the other side would affect the result so seriously. And the para C-H bond is not taken into account, for the spin density of the para proton derived by the direct and in-plane interaction would be relatively small and its order of magnitude would be able to be estimated by the above calculation.

The change of the hybridization of the carbon C_1 is not taken into consideration, for the change of the hybridization does not seem to affect the results. The C_1 - C_{ortho} bond

length is fixed to be 1.39Å and the C₀-C₁-C₀ angle 120°. As the elongation of the bond C₁-C_{ortho} would reduce the coupling, as we saw in the previous section, the result of this calculation gives the maximum magnitudes of the coupling constants.

Canonical Structures and Integrals.-----All of the independent canonical structures that have the maximum bonding number, five structures in all, are taken as bases of the calculation, which are shown in Fig. 5. Ionic structures are not included in the calculation at all. Integrals are evaluated by the same methods as in the preceding section.

Calculation Result.-----Normalized ground state wave function is obtained as follows:

$$\begin{aligned} \Psi = & 1.1338 \phi_1 + 0.0968 \phi_2 + 0.1144 \phi_3 + 0.0673 \phi_4 \\ & + 0.1779 \phi_5 \end{aligned} \quad (3)$$

where ϕ_i is the i th canonical structure (as to the numbering of them, see Fig. 5). From this function is derived the spin density in Fig. 6. The spin density is almost completely localized on the non-bonding hybridized orbital, n , on the carbon C₁; phenyl radical may be said to be essentially a localized radical. From the spin densities in Fig. 6 are calculated the coupling constants of ortho and meta protons

with Eq. 2. The result is shown in Table III.

§4. Assignment of Observed Spectra and Discussion

On inspection of the calculated proton coupling constants of cyclohexadienyl radical $C_6H_7\cdot$, the complex spectrum, the triplet with finer structures of four triplets, observed by Ohnishi et al. and by Fischer may safely be assigned to cyclohexadienyl radical (see Table II). Agreement with the observed and the calculated spectra seems to be very good.* Though the coupling constant of methylene protons depends on the $C\beta-C_{ortho}$ bond length, the coincidence with the experimental value 47.5~50.0 gauss is accomplished at the bond length between 1.54Å (C-C single bond) and 1.39Å (C-C bond in benzene). This would be rational in cyclohexadienyl radical, for it is produced from the regular hexagonal benzene molecule by hydrogen addition.

On the other hand, according to the theoretical results in Table III, phenyl radical is considered to give a triplet with finer triplet structures. The singlet spectrum observed by Ohnishi has the width of 25 gauss between the maximum

* The coupling constant calculated for meta protons is a little too large. This seems to be the general trend or defect of the simple valence bond calculation of conjugated system.

slopes and, depending on conditions, has slight nicks, showing it might be a triplet. The large width just corresponds to the unresolved hyperfine structures of the theoretically predicted splittings of 12 gauss. Thus this broad singlet spectrum may safely assigned to phenyl radical. ЧХЕИДЗЕ's assignment, in which the largest coupling constants 45 gauss is attributed to ortho positions of phenyl radical, does not correspond to the theoretical result at all. His spectrum which is alike to Ohnishi and Fischer's would have to be ascribed to cyclohexadienyl radical.

In this manner the assignment of the two kinds of the observed ESR spectra from irradiated benzene seems to be decided by the aid of this valence bond calculation.

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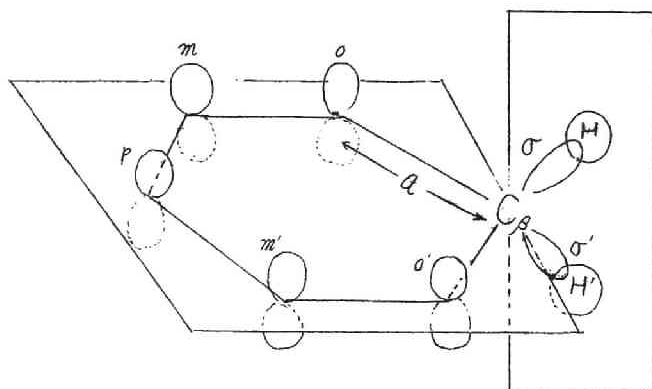


Fig. 1 Model of C_6H_7 Radical

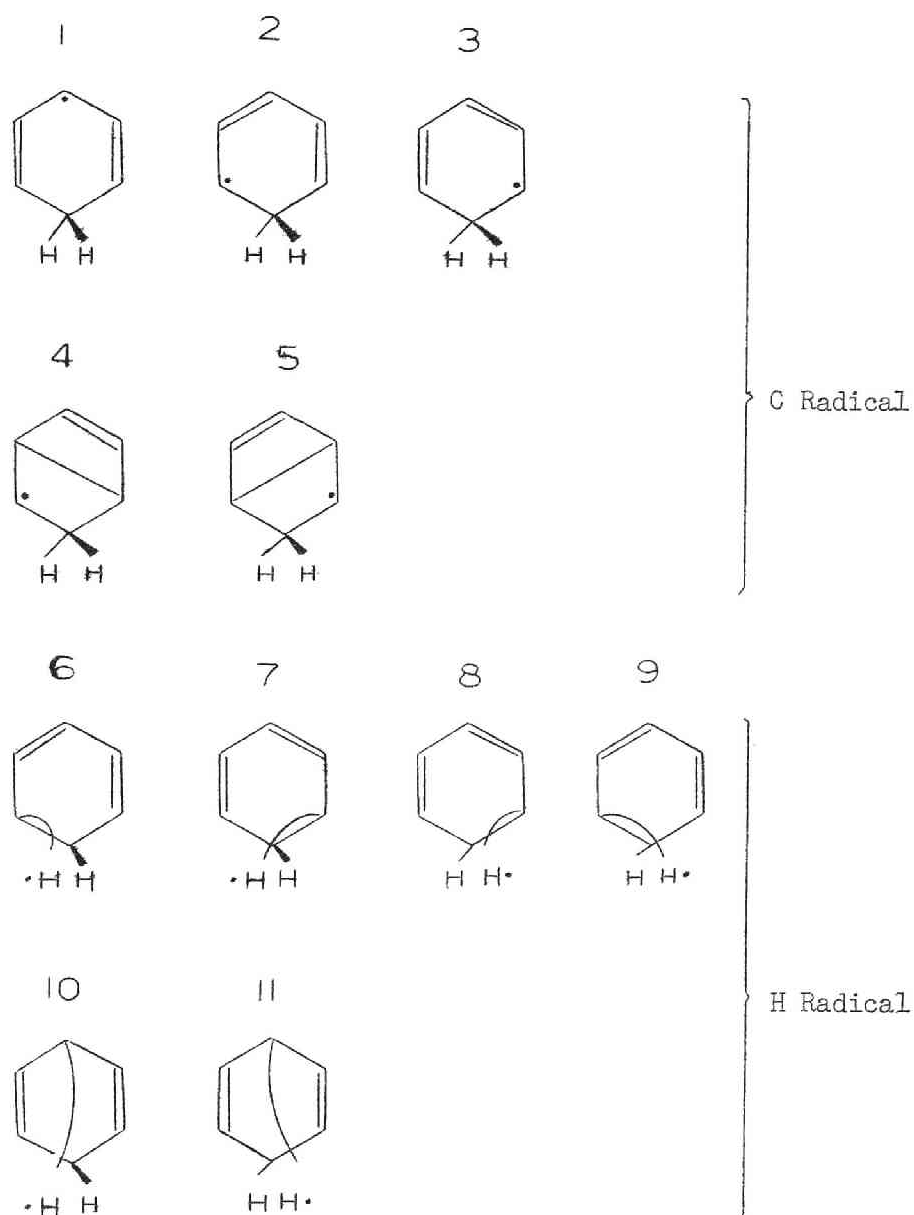


Fig. 2 Canonical structures taken into calculation of C_6H_7 .

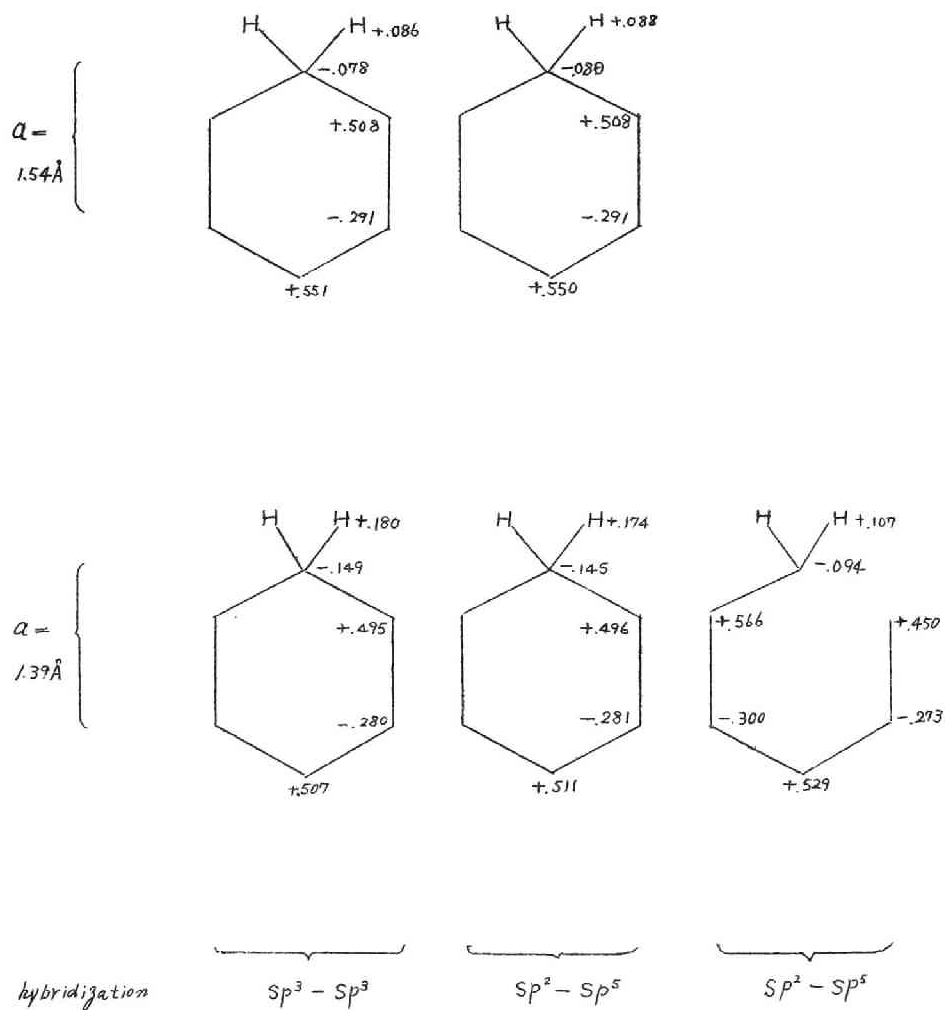


Fig. 3 Calculated spin density of $C_6H_7\cdot$ radical

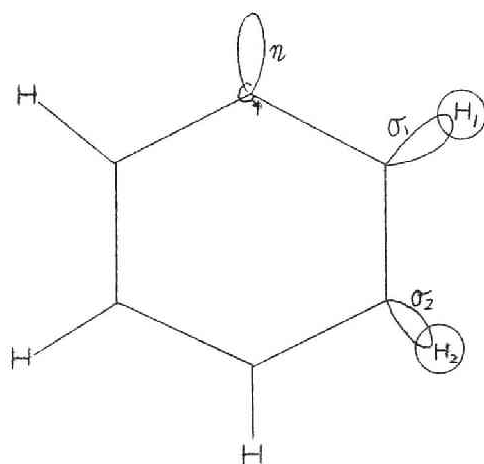


Fig. 4 Model of $C_6H_5^\bullet$ radical

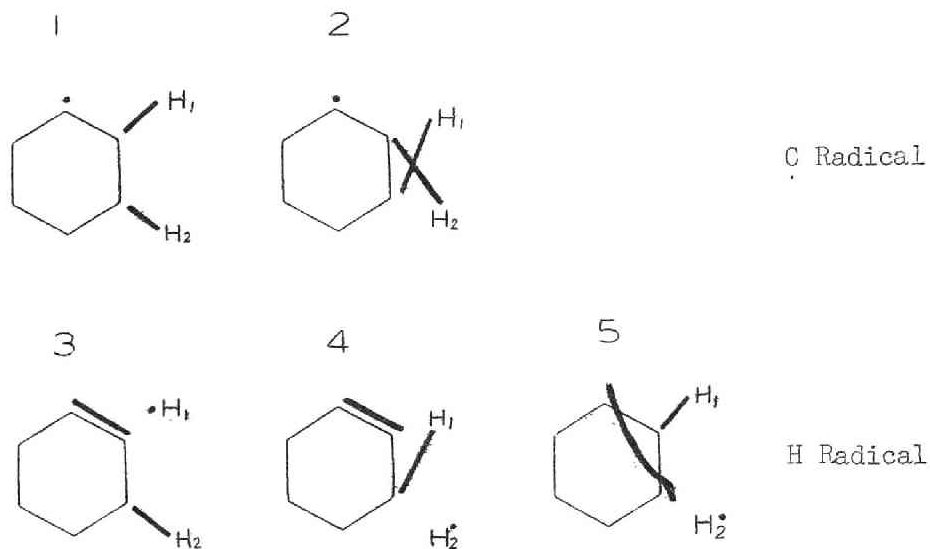


Fig. 5 Canonical structures taken into calculation of $C_6H_5^\bullet$.

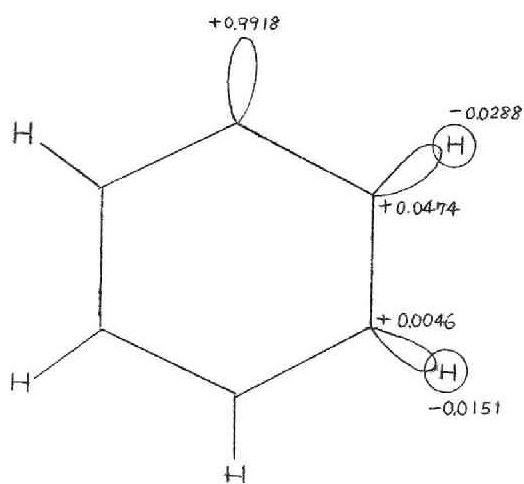


Fig. 6 Calculated spin density of
 $\text{C}_6\text{H}_5\cdot$ radical

Table I Coefficients of Canonical Structures in the Ground State Wave Function of C_6H_7 .

Hybridization of Carbon C_1	C_1-C_{ortho} distance	Coefficients				
		C_1	C_2, C_3	C_4, C_5	C_6, C_7, C_8, C_9	C_{10}, C_{11}
sp^3-sp^3	1.54Å	+0.3955	-0.3118	+0.0986	+0.0572	+0.0055
sp^2-sp^5	1.54Å	+ .3951	- .3100	+ .0993	+ .0584	+ .0053
sp^3-sp^3	1.39Å	+ .3737	- .2499	+ .1058	+ .1152	+ .0093
sp^2-sp^5	1.39Å	+ .3752	- .2537	+ .1051	+ .1118	+ .0086

Table II Calculated and Observed Proton Coupling Constants of $C_6H_7\cdot$ Radical

Isotropic Coupling Constant (in gauss)

Proton	Calculated ^{b)}		Observed	
	$a=1.54\text{\AA}$	$a=1.39\text{\AA}$	Ohnishi ²⁾ & Fischer ¹⁾	$\Psi \times \text{EINDBE}^{4)}$
ortho	-11.4	-11.1~11.2	10.4~10.6	10.2 (meta) ^{a)}
para	-12.4	-11.4~11.5	10.4~10.6	10.2 (para) ^{a)}
meta	+ 6.5	+ 6.3	2.5 ~ 2.6	--
methylene	+36~37	+73~76	47.5~50.0	45.2 (ortho) ^{a)}
spectrum (lines)	3x4x3	3x4x3	3x4x3	3x4 (Assigned to $C_6H_5\cdot$)

a) Assignment by $\Psi \times \text{EINDBE}^{4)}$. . Assigned to $C_6H_5\cdot$ Radical.b) No matter what the hybridization of C_β is.

Table III Calculated and Observed Proton Coupling
 Constants of C_6H_5 Radical

Proton	Coupling Constant (in gauss)		
	Calculated	Observed	
		Ohnishi ²⁾	ЧХЕНДБЕ ⁴⁾
ortho	-12.1	----	45.0
meta	- 6.3	----	10.2
para	---	----	10.2
spectrum (lines)	3x3x2	1 ($\Delta H_{msl} \simeq$ 25 gauss)	3x4

Chapter 10

Valence Bond Calculation of Spin Densities of Various Hydrocarbon Radicals in a Simplest Approximation

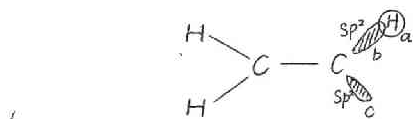
§1. Introduction

Experimental ESR studies on various organic radicals have been recently performed and also now in progress in a rapid pace. Assignment of observed spectra to the actual radicals would be very difficult without the help of theoretical considerations. Especially calculated spin density often makes it easy to correlate experimental results to the electronic structures of radicals. In this sense precise calculation on all of possible radicals are anticipated, on which, though the computer technique has given a great facility, numerical calculations seems to be actually impossible.

In the present stage it would not be meaningless to make a simplest approximation so as to be able to calculate spin densities of various radicals---especially proton spin density---with ease and without any more solving secular equations. In this chapter we would like to estimate the proton coupling constant in various radicals in the simplest approximation as is stated above.

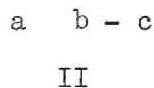
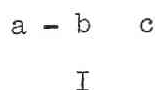
§2. Approximation and General Results

Consider a radical and the proton which is in it and is now under discussion on the hyperfine coupling constants. We simply take the radical as a three-electron and three-atomic-orbital problem, consisting the atomic orbital c and the $a - b$ bond, c being the atomic orbital where the odd electron is located in the classical structure, and a being the proton in question and b being the atomic orbital bonding to a . This is the simplest model for estimating the spin density on the proton a . For example, if we want to know the spin density on the α -proton of the following imaginary radical, a , b and c should be such as shown in the figure.



Ignoring the other atomic orbitals and the other electrons in the radical corresponds to the approximation that we are going to estimate only the direct interaction of the $a - b$ bond with the electron on c , but that we neglect mixing of the interaction between the electron c and other electrons and that between the latter and the $a - b$ bonds.

For this three-electron system the following two canonical structures with maximum bondings are possible.



Ionic structures, of which those such as C^-H^+ might be most important because of the difference of electronegativity of C and H, are thoroughly neglected for the sake of simplicity.

Neglecting atomic overlap integrals, we are led to the following matrix elements between canonical structures.

$$\left. \begin{aligned} H_{II} &= Q' + \frac{3}{2}(ab) & S_{II} &= 1 \\ H_{III} &= Q' + \frac{3}{2}(bc) & S_{III} &= 1 \\ H_{II} &= -\frac{1}{2} \left[Q' + \frac{3}{2}(ab) + \frac{3}{2}(bc) - \frac{3}{2}(ac) \right] & S_{II} &= -\frac{1}{2} \end{aligned} \right\} \quad (1)$$

where

$$Q' = Q - \frac{1}{2}(ab) - \frac{1}{2}(ac) - \frac{1}{2}(bc) \quad (2)$$

and Q is the coulomb integral:

$$Q = \int a(1) b(2) c(3) H^* a(1) b(2) c(3) d\tau \quad (3)$$

(H^* total hamiltonian)

and (ij) is the exchange integral between the orbitals i and j , with k unexchanged:

$$(ij) = \int i(1) j(2) k(3) H j(1) i(2) k(3) d\tau \quad (4)$$

Here, putting γ and β as follows:

$$\left. \begin{aligned} \gamma &= (bc) - (ac) \\ \beta &= (bc) - (ab) \end{aligned} \right\} \quad (5)$$

and furthermore

$$\beta / \gamma = \beta \quad (6)$$

the following ground state energy, E , and the ground state spin density on the atom a , ρ_a , and that on the atomic orbital b , ρ_b , are obtained.

$$E = Q^* + \frac{1}{3} \left[2B - 1 \pm 2\sqrt{B^2 - B + 1} \right] \quad (7)$$

$$\rho_a = \left\{ (4B^2 - B + 1) \pm (4B + 1)\sqrt{\gamma} \right\} / 3 \left\{ 2\gamma \pm (2B - 1)\sqrt{\gamma} \right\} \quad (8)$$

$$\rho_b = \left\{ (4B^2 - 7B + 4) \pm (4B - 5)\sqrt{\gamma} \right\} / 3 \left\{ 2\gamma \pm (2B - 1)\sqrt{\gamma} \right\} \quad (9)$$

$$\gamma = B^2 - B + 1$$

as simple functions of the parameter B .

In Eqs. 7, 8 and 9, the upper sign should be employed for $\gamma < 0$ and the lower for $\gamma > 0$.

In our cases the integral (ab) is negative and the largest in magnitude because a and b is bonded in the classical structure, and therefore the parameter β is limited to be plus. Thus the sign of B gets equal to the sign of γ . So far as we consider C-H bond as the bond $a - b$, (ab) is estimated of the order of $-4 \text{ eV.}^{1)2)}$ Setting $(ab) = -4 \text{ eV}$, the parameter B is written as a function of (bc) and (ac) , as shown in Fig. 1. As in most cases (bc) is between -2 eV and

+2eV and (ac) is between -3 eV and +3 eV (shadow lines in the figure), the probable value of B may be in the ranges $B < -1/4$ and $B > 1$.

Calculated spin density³⁾ on the atom a is tabulated in Table I and are plotted against the parameter B in Fig. 2. It is clear that negative spin density⁴⁾ on the orbital a is achieved by the positive value of B , that is, by the relation $(bc) > (ac)$.

Using Table I and appropriately evaluated three exchange integrals and also interpolating the values in it, one who wants to roughly estimate the spin density on a proton can easily obtain what he wants, which gives rise to the proton isotropic hyperfine coupling constant. By Eq. 9 is calculated spin density on carbon and, consequently, the anisotropic coupling constant⁵⁾ on the proton and a part of the isotropic coupling of the carbon isotope.

The merits that Eqs. 8 and 9 for estimating spin densities are extraordinarily simple turns into the demerits that the numerical results severally depend on the choice of exchange integrals. Unfortunately there seems no reliable method of evaluating these integrals.^{1,2)} In spite of this unreliability of the numerical values obtained, this simplest method seems to be useful for such purpose as to know whether

the coupling constant of a proton is 100 gauss or zero.

83. Some Examples

In this section application of Eq. 8 would be given to some hydrocarbon radicals, of which some are actually known and others are imaginary.

Exchange integrals are calculated tentatively according to the method of van Vleck⁷⁾ and Karplus et al.⁶⁾ and partially of Altman.⁸⁾ In the method C-H exchange integrals are estimated from the dissociation energy of methane and some other properties, carbon one-center integrals are from spectroscopic data of carbon atom and two-center C-C exchange integrals are based on the effective two electron hamiltonian. For various hybridizations of carbon atoms the C-H and the C-C bond lengths are not varied.

If the spin density, ρ_H , on the proton in question is calculated by Eq. 8, the proton isotropic coupling constant, a_H , is derived as follows:

$$a_H = Q \rho_H \quad (10)$$

In Eq. 10 Q is given theoretically to be 507 gauss, but because of the uncertainty of exchange integrals employed in this section and of the effect of neglecting ionic structures

theoretical value does not seem to fit experiments well: in our previous calculation¹⁾ on CH₂ group 420 gauss is known to be preferable for the same sets of exchange integral parameters as in this section.

Example 1. So-called σ - π interaction³⁾ between an odd electron on the $p\pi$ orbital of a carbon atom and the C-H bonding electrons, hybridization of the carbon being sp^2 (see Fig. 3). Exchange integrals are calculated as follows:

$$(ab) = -3.916 \text{ eV}$$

$$(bc) = -0.959 \text{ eV}$$

$$(ac) = -0.600 \text{ eV}$$

Thus $B = +13.58$ from Eqs. 5 and 6, and ρ_H is equal to -0.0375. The proton coupling constant is, therefore, -19.0 gauss or -15.8 gauss, the former being from 507 gauss as Q and the latter from 420 gauss. Agreement with experimental result, -22 to -23 gauss,³⁾ is pretty good for the rough approximation.

Example 2. σ - π interaction, but the hybridization of the carbon atom is not sp^2 but sp . (Fig.4) The purpose of the example is to see how the hybridization of the carbon orbital in the C-H bond effects the hyperfine structure. Results are as follow: $(ab) = -3.970$, $(bc) = +1.323$ and $(ac) = +0.600 \text{ eV}$; $B = +7.320$, $\rho_H = -0.0702$ and a_H is -36.0 gauss or -29.5

gauss.

Such a partial structure as in Fig. 4 will be accomplished by anions or cations of acetylene derivatives, for instance, of acetylene and of phenyl acetylene. In these cases proton coupling constant should not be connected to the spin density on the $p\pi$ orbital of the adjacent carbon simply with the following equation for sp^2 system:

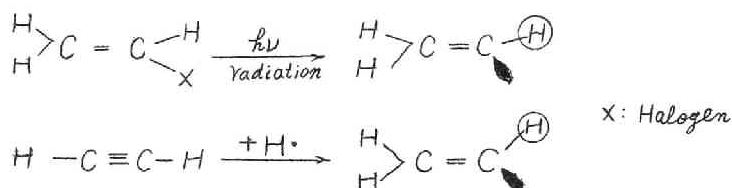
$$a_H = -22.5 \rho_C \quad (12)$$

but with the equation in which the proportionality factor is more negative.*

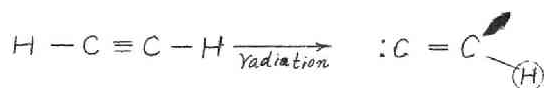
Example 3. Two sp^2 hybridized orbitals on a carbon atom and a hydrogen atom bonded to one of them, as are shown in Fig. 5. Results are: $(ab) = -3.916\text{eV}$, $(bc) = +1.455\text{eV}$ and $(ac) = -0.492\text{eV}$; $B = +2.759$ and $\rho_H = -0.185$. The proton coupling constant is therefore -93.6 gauss or -77.7 gauss.

One of the radicals which might have any possibility to have such partial structure in the ground state would be vinyl radical, though its ESR spectrum has never been observed.

*When the hybridization of a carbon is changed, will change other factors than mentioned above, such as the polarity of the C-H bond and the bond distance of the bond. The change of the polarity from $sp^2\text{C-H}$ to $sp\text{C-H}$ will make ρ_a more positive and the change of the bond length makes it more negative. These two factors thus seem to compensate each other.



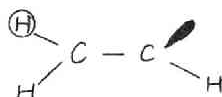
Another one would be acetenyl radical, though the structure of the radical has never decided to be linear or bent.



Ohmishi et al.⁹⁾ have recently observed a doublet (splitting is as large as 129 gauss) signal of ESR of a radical which is produced by UV irradiation on phenyl acetylene and is tentatively attributed to acetenyl radical $\cdot\text{CCH}$. The splitting is surprizingly large in comparison with the result of this example calculation. Similar experimental results were obtained for formyl radical,¹⁰⁾ which is known to be bent as in Fig. 6 and the proton coupling constant is 137 gauss.

Example 4. An odd sp^2 electron on α carbon and a sp^3 C-H bond on β carbon, which are directed to the same direction of the C-C axis. (Fig. 6). Results are: $(ab) = -3.916$, $(bc) = +0.290$ eV and $(ac) = 0$ (assumed); and $B = +14.50$ and $\rho_H = -0.0351$ and therefore $a_H = -17.8$ gauss or -14.7 gauss. This is in good agreement with the spin density on o-proton in phenyl radical, which was calculated previously

by the present authors²⁾, proving this simplest approximation to be reliable. Another proton which corresponds to this example is one of the β -protons in vinyl radical:



Similarly one might easily know the approximate value of spin density on any proton and any orbital bonded to the proton by the aid of Eqs. 8 and 9.

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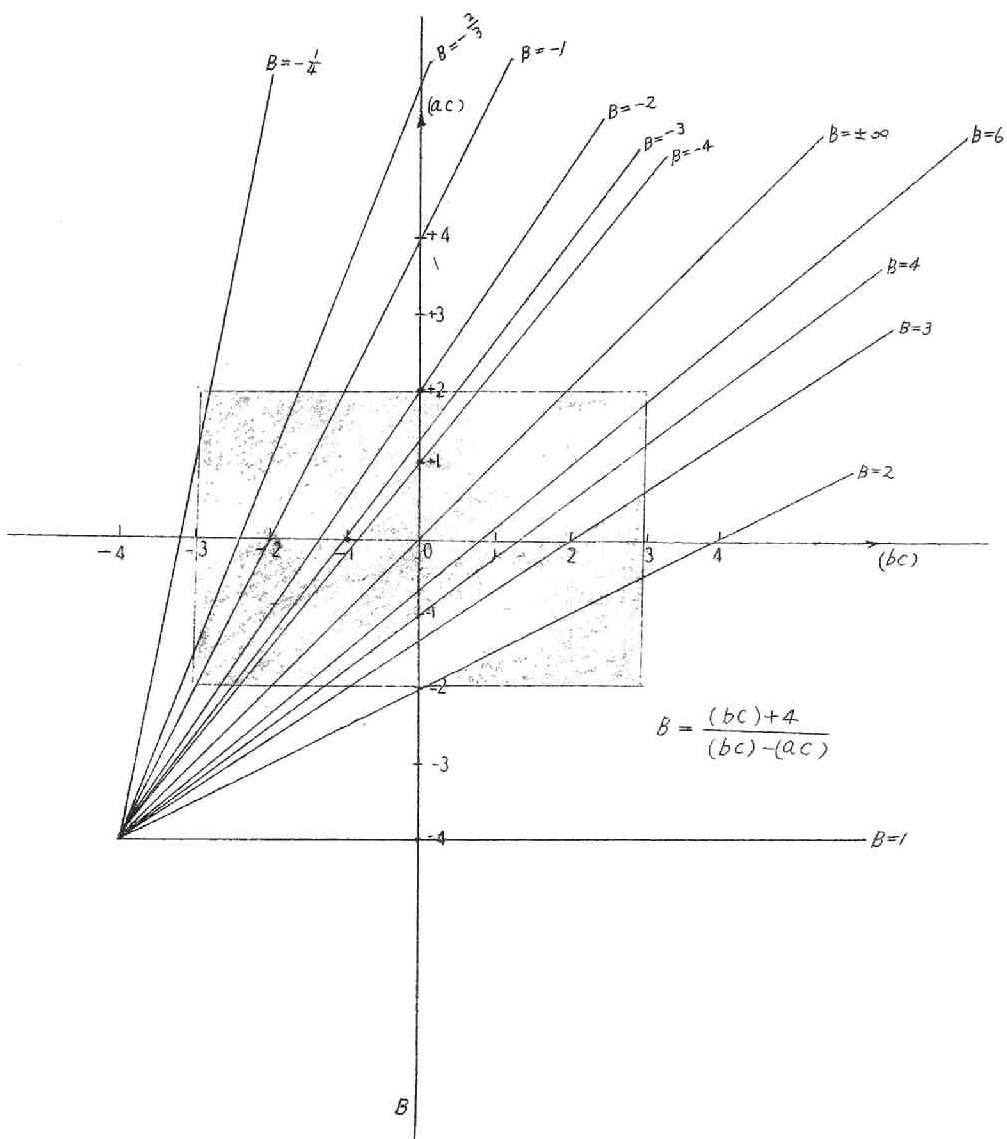


Fig. 1 B as a function of (bc) and (ac)

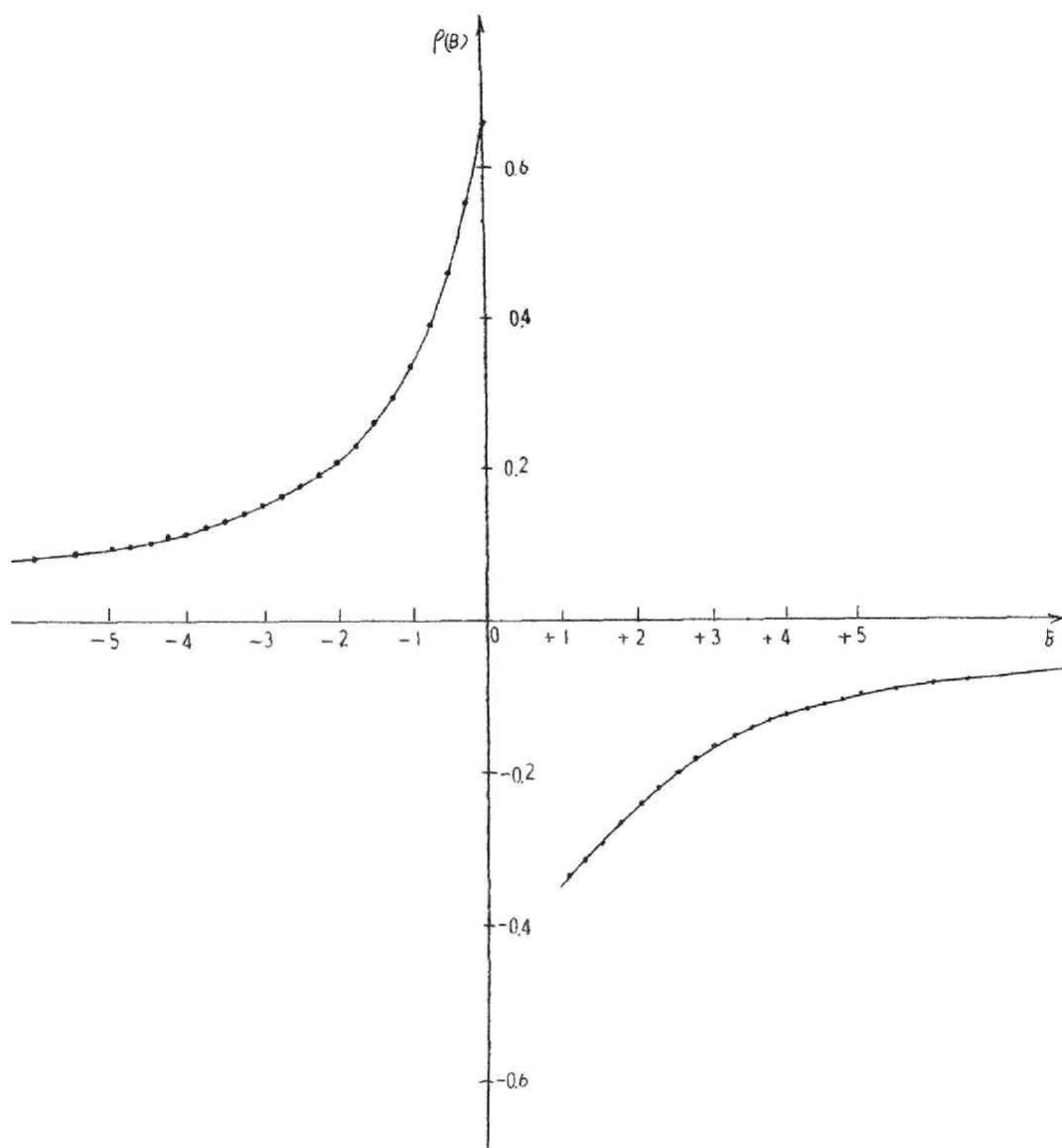


Fig. 2 Spin density on atom a as a function of parameter B.

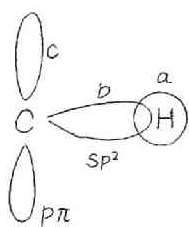


Fig. 3

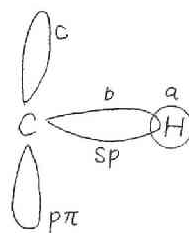


Fig. 4

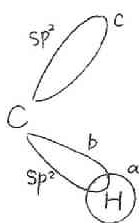


Fig. 5

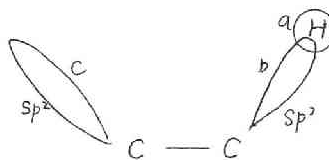


Fig. 6

Table I Spin Density on Atom a as a Function of Parameter B

B	ρ_a	B	ρ_a	B	ρ_a
- 0	+0.6667	-11.0	+0.0443	+ 5.5	-0.0936
- 0.25	.5516	-12	.0407	+ 6.0	.0858
- 0.50	.4593	-13	.0376	+ 6.5	.0791
- 0.75	.3881	-14	.0350	+ 7.0	.0733
- 1.00	.3333	-15	.0327	+ 7.5	.0684
- 1.25	.2907	-16	.0307	+ 8.0	.0640
- 1.50	.2569	-17	.0289	+ 8.5	.0602
- 1.75	.2296	-18	.0274	+ 9.0	.0568
- 2.00	.2073	-19	.0259	+ 9.5	.0536
- 2.25	.1888	-20	.0247	+10.0	.0510
- 2.50	.1732			+11	.0463
- 2.75	.1599	+ 1.00	-0.3333	+12	.0424
- 3.00	.1484	+ 1.25	.3213	+13	.0391
- 3.25	.1385	+ 1.50	.2966	+14	.0363
- 3.50	.1297	+ 1.75	.2695	+15	.0338
- 3.75	.1220	+ 2.00	.2440	+16	.0317
- 4.00	.1151	+ 2.25	.2215	+17	.0298
- 4.25	.1090	+ 2.50	.2020	+18	.0281
- 4.50	.1034	+ 2.75	.1851	+19	.0266
- 4.75	.0984	+ 3.00	.1706	+20	.0253
- 5.00	.0939	+ 3.25	.1580		
- 5.5	.0859	+ 3.50	.1471		
- 6.0	.0792	+ 3.75	.1374		
- 6.5	.0734	+ 4.00	.1289		
- 7.0	.0684	+ 4.25	.1214		
- 7.5	.0641	+ 4.50	.1146		
- 8.0	.0602	+ 4.75	.1086		
- 8.5	.0568	+ 5.00	.1031		
- 9.0	.0538				
- 9.5	.0511				
-10.0	.0486				

CLOSING

In the present thesis the author tried quantum chemical approaches to complicated phenomena in organic chemistry. In Part I approaches were carried out in the field of chemical reactivities. By calculating the existing reactivity indexes in higher approximations, total π electron density and free valence, the indexes in the static method, are proved not to deserve measures of reactivities. He also obtained mathematical interrelations and pointed out physical differences between the frontier electron theory and the Z value. These discussion would be an approach to the real mechanism of the aromatic substitution reaction. The molecular orbital treatment of reaction of excited molecules stressed the importance of the frontier levels in such reactions. In the study on antioxidants possibilities of several models of the transition state were tested from the view points of both the σ and the π electronic structures.

In Part II by the aid of the LCAO MO method for σ electro some physicochemical properties of conjugated halogenated hydrocarbons were discussed. The presumption that in these compounds the lowest σ unoccupied level might be lower than the lowest π unoccupied level was deduced in these studies and it was ascertained by a higher approximation. Studies

on ESR spectra were carried out mainly in connection with proton coupling constants. Assignment of experimental spectra of terephthalaldehyde anion, phenyl and cyclohexadienyl radicals was established first by these theoretical calculations. The study on the angular dependency of CH_2 proton couplings, which was against the current interpretation, has an important meaning in connection to the structure of radicals. A simplest method, which was presented for calculating proton couplings, would enable any one to predict easily the patterns of any hydrocarbon radical.

